Universidade de Aveiro
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Departamento de Engenharia Mecânica

José Miguel Teixeira Margarido

Desenvolvimento de novos materiais naturais nanocompósitos para aplicações em engenharia

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Mecânica, realizada sob a orientação científica de Ricardo José Alves de Sousa, Professor Auxiliar com Agregação no Departamento de Engenharia Mecânica da Universidade de Aveiro e Paula Alexandrina de Aguiar Pereira Marques, equiparada a Investigador Principal no Departamento de Engenharia Mecânica da Universidade de Aveiro.

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Palavras-chave

Cortiça aglomerada; testes mecânicos; absorção de energia; grafeno; oxido de grafeno; nanocompósitos; biopolímeros.

Resumo

A crescente e generalizada consciencialização ambiental obriga cada vez mais a incutir o uso de materiais compatíveis com a sociedade onde nos inserimos. A cortiça é 100% orgânica e sustentável pelo facto de um só sobreiro conseguir produzir cerca de 20 vezes esta matéria prima ao longo do seu ciclo de vida. Também na ótica da reciclagem, todas as sobras das diversas indústrias que usam a cortiça podem fazê-lo, sendo esta triturada e aglomerada posteriormente através de resinas. Porém, é precisamente neste capítulo que residem alguns obstáculos na amizade com a ecologia. O aglomerado de cortiça é bastante apetecível ao nível do preço, quando comparado com o seu estado puro, e uma vez que mantém grande parte das vantagens e competências iniciais, não é de estranhar que seja usado não só em rolhas para vinhos de consumo rápido, mas também em inúmeras aplicações como isolamento térmico e acústico, absorvedor de impactos, peças de vestuário, objetos de design, entre outros. Todavia, a maioria do aglomerado é formado por cola que não é biodegradável, o que vai contra uma das principais bandeiras deste nobre produto português.

Pretende-se com esta dissertação caminhar para atenuar esta tendência. Para isso, foi confecionado um aglomerado de cortiça com uma resina 40% biológica e testadas as propriedades mecânicas em testes de compressão quase-estáticos e de impacto.

Ainda no decorrer desta tese, foi criado um nanocompósito de aglomerado de cortiça e grafeno, com o intuito de melhorar as propriedades mecânicas do aglomerado.

De acordo com os resultados alcançados foi possível demonstrar que é possível aprimorar a cortiça em duas frentes diferentes. Por um lado, é possível conceber um aglomerado utilizando resinas mais amigas do ambiente e aplica-lo sem que se percam as suas propriedades essenciais. Por outro, a adição de grafeno como material de reforço foi validada no que diz respeito às propriedades mecânicas do compósito final.

Keywords

Agglomerated cork; mechanical tests; energy absorption; graphene; graphene oxide; nanocomposites; biopolymers.

Abstract

The increasingly general environmental responsibility progressively encourages the use of materials compatible with the reality where we live. Cork is 100% organic and sustainable since one cork tree can produce about 20 times this raw material throughout its life cycle. Also from the recycling point of view, all leftovers from the various industries that use cork can put it in practise to create by-products, triturating them and then agglomerating through a binder. However, it is precisely in this chapter that there are some complications in this friendship with ecology. The agglomerate is very attractive due to its price when compared to the pure state, and since it keeps many of the initial advantages and competencies, it is not surprising that it is used not only in corks for fast-consuming wines, but also in numerous applications such as thermal and acoustic insulation, impact absorption, garments, design objects, among others. However, most of the agglomerate is composed by resins that are not biodegradable, which goes directly against one of the main flags of this noble Portuguese product.

It is intended with this dissertation to attenuate this tendency. To this end, a cork agglomerate with a 40% biological resin was prepared and the mechanical properties were tested in quasi-static and impact compression tests.

Also in the course of this thesis, a nanocomposite of agglomerate of cork and graphene was created, in order to improve the mechanical properties of the agglomerate.

According to the results achieved it was possible to demonstrate that cork can be improved on two different fronts. On the one hand, it is possible to design an agglomerate using environmental glues and apply it without losing its essential properties. On the other hand, the addition of graphene as reinforcing material was validated with respect to the mechanical properties of the final composite.

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Chapter 1
State of the Art

1.1 Introduction

Cellular materials have been finding increasing curiosity as a solution for many engineering applications. They have a huge potential that is not fully exploited yet, and can be distinguished in categories such as: natural, synthetic, open cell and closed cell (Gibson and Ashby, 1997). They show a mixture of unique properties such as good thermal and acoustic insulation, high stiffness, high energy absorption capacity and high yield stress with respect to their mass. Factors like these make them thought-provoking in many practical uses such as packaging, aerospace industry and for structural applications (Alcântara et al. 2013; Paulino and Teixeira-Dias, 2011).

In order to develop a direction towards an objective it's important to have the following statement present in mind: "The best material for each application depends on the application itself" (Fernandes et al. 2015). Which, applied to cellular materials, means that there are variations such as strain and mechanical loading that will lead to an optimal choice inside this big family materials. As an example, EPS (expanded polystyrene), that thanks to its price it is considered to be the most widespread of the synthetically group, has an excellent first impact performance. Nevertheless, the material deforms without recovering elastically. The consequence of this circumstance is that it is not viable to use it in road helmets (where, for instance cork can shine), but fits perfectly the packing industry (Shuaeib et al. 2007; Shuaeib et al. 2002; Gilchrist and Mills, 1994).

Many researchers have been attracted by cork mainly due to its capacity to absorbing energy. The variety of new possible applications are abundant and to accomplish that there are already various studies that explored the central aspects of its mechanical aspects (Fortes and Teresa, 1989; Gibson et al. 1981; Pereira et al. 1992; Rosa and Fortes, 1988).

The main objective of this study is to validate a graphene nanocomposite that can show up as an upgrade to agglomerated cork and its mechanical properties and, in the other hand, build an agglomerated cork made of an environmental friend binder.

1.2 Cellular Materials – Mechanical properties

"When modern man builds large load-bearing structures, he uses dense solids: steel, concrete, glass. When nature does the same, she generally uses cellular materials: wood, bone, coral. There must be good reasons for it" (Gibson, 2015).

If there is the desire of having good mechanical properties at low weight, cellular structures are the most natural choice. As previously said, these materials appear oftentimes in nature and have many potential to engineering applications (Fratzl and Weinkamer, 2007). The way they are structured in our reality can serve inclusively as inspiration for our goals. An example of this kind of use by man is some lightweight aerospace components that employ honeycomb-like materials as illustrated in Figure 1.1.

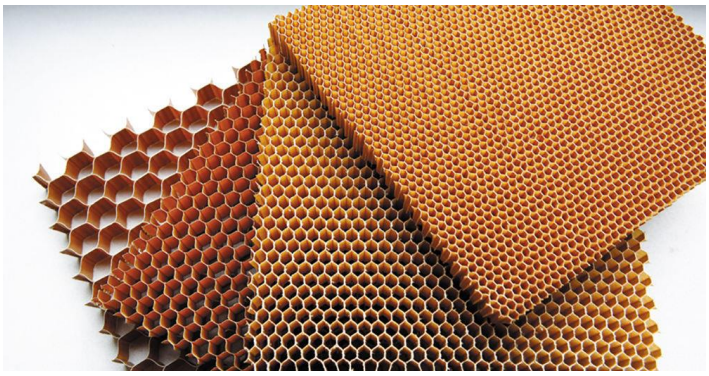

Figure 1.1: Honeycomb aluminium / fiberglass / aramid paper / for the aeronautics industry (Aeroexpo, 2017).

Analysing a cellular material considering its stress-strain curve allow to identify three main regimes as illustrated in Figure 1.2

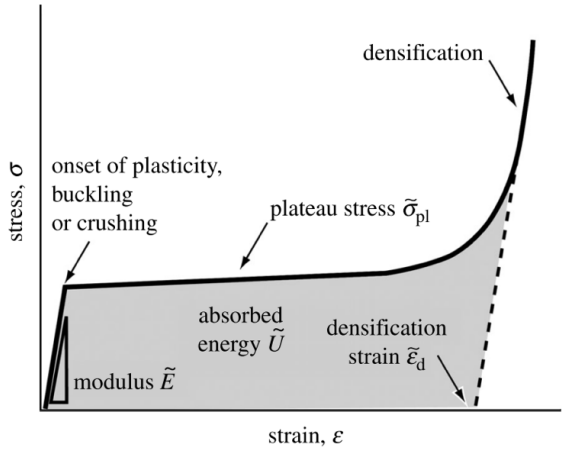

Figure 1.2: Cellular solid's stress-strain curve (Ashby, 2006).

The onset of plasticity (a), the plateau stress (b) and the densification (c). The first one corresponds to cell edge bending or face stretching (Figure 1.3).

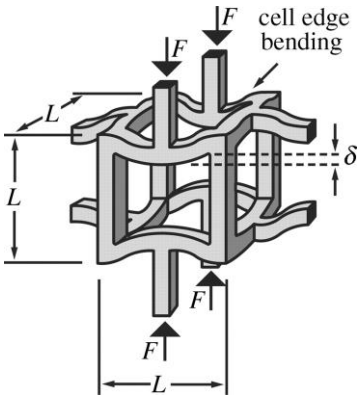

Figure 1.3: Cell bending due to a load structure (Ashby, 2006).

To a small amount of strain, the material deforms in a linear elastic way. Then a period of progressive cell collapse by elastic buckling, starts plastic yielding or brittle crushing called plateau stress. At this time, the material can handle additional deformation and keep the same value of stress, a feature that pleases engineering (Cantor et al. 2008).

It's also possible to get this phase if the material of the cell wall has its plastic limit immediately next after the elastic limit. In this case, the rupture point is achieved. For instance, one good practical example are the ceramic foams, which because of its fragility to fracture are incapable to return to their initial position after deformation (Figure 1.4).

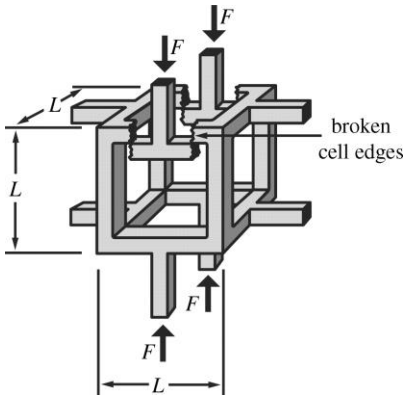

Figure 1.4: Example of a brittle foam collapse (Ashby, 2006).

Finally, the densification takes place when the cell collapse ends, since the opposite cell walls come into contact.

Often cellular solids have low relative densities and can still handle a considerable strain before densification happens. As long as the strain growths, the cells become more struggled along the loading direction, which increases the toughness/stiffness of the material until tensile failure occurs. There is a small deformation comparing with the values of stress that brutally emerge (Gibson 2005).

1.3 Cork

"I no sooner discerned these (which were indeed the first microscopical pores I have ever saw…) but me thought I had with the discovery of them, perfectly hinted to me the true and intelligible reason for all the phenomena of cork" (Hooke, 1665).

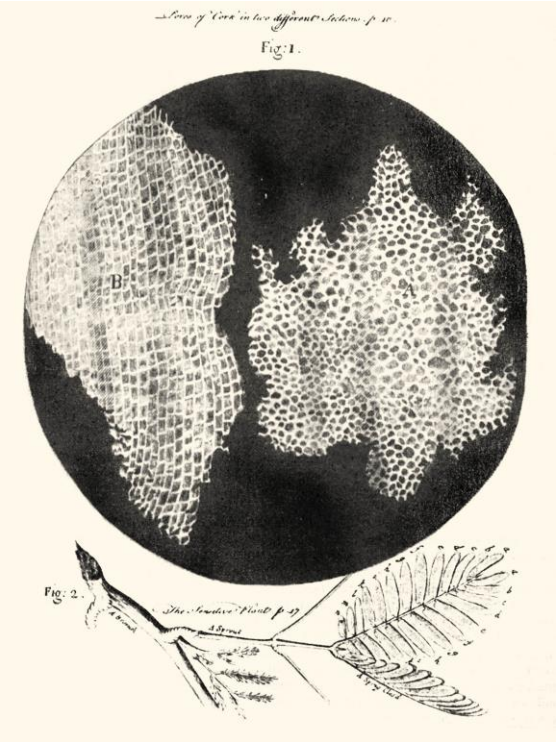

Figure 1.5: Micrographia's book (Hooke, 1665).

Cork, which is known to be intimately connected to the cell birth, is the bark (Figure 1.6) of the cork oak (*Quercus suber L*).

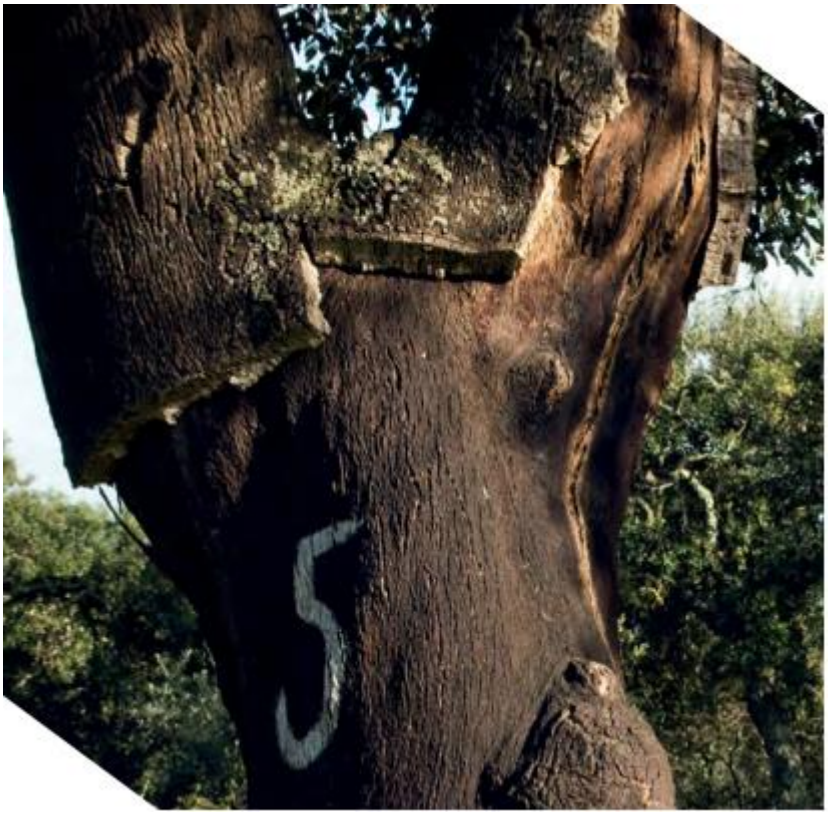

Figure 1.6: Cork oak and its bark (Amorim, 2017).

Macroscopically, it is a lightweight, elastic, acoustic absorber, thermal and electrical insulation and nearly impermeable to fluids. The thickness of the cork planks is between 2 and 5 centimetres depending on the years of growth and its conditions. Biologically speaking, it is an undifferentiated cell reproduced by a cellular tissue with capacity for cell division called phellogen. When the cork is extracted, the phellogen dies but it can regenerate due to its meristematic capacity. This process allows to differentiate three types of cork accordingly with the respective generation. The so-called virgin cork takes place after the first harvest which usually happens when it reaches the first 20-30 years of life. Despite the poor quality obtained (which is justify due to its irregular structure, thickness and density and being, for the reasons presented below easy crumbly), it is used to produce agglomerate, applied on shoe soles, gaskets, etc. The second generation (*secundeira in Portuguese*) does not achieve the best potential of the cork oak. To get there, it is necessary to wait 40-50 years of its lifetime. From that point on the tree can be harvested every 9 years until its death (generally

adding up 100-150 years) and the last type of cork pops up – the gentle cork (*amadia in Portuguese*) that is used in every purpose that relies on homogeneous cork being the best example the cork stoppers.

In the winter, the phellogenic tissue stops to grow and that can be verified by the dark zones. However, in the beginning of the spring the phellogenium period occurs and it is present until October somewhere around here the harvest should (when necessary) happen.

After being harvested, the water loss through the surface is increased, which reduces the biological activity of the tree (Fortes et al. 2006).

1.3.1 Cork Structure

Cork is fully natural, with unique properties which sets it an unparalleled character. It is lightweight since more than 50% of its volume is air and weights 0,2 g/cm^3 meaning that it floats. This feedstock is not only impermeable to liquids and gases but also presents resistance to moisture (Figure 1.7). It is elastic and compressible with the feature of being a solid that, when compressed on one side, does not increase the volume on the other, due to null Poisson ratio (Figure 1.8).

Figure 1.7: Boats with the hull in cork (Amorim, 2017).

Figure 1.8: Insole made of cork (Amorim, 2017).

Due to cork's low conductivity to heat, it's thermal and acoustic insulator (Figure 1.9). Cork is resistant to impact and has a high friction coefficient provided by the honeycomb structure. It is hypoallergenic since does not accumulate dust and, in addition to all of this, it is fully biodegradable, renewable and recyclable, fire retardant and has a great and natural touch (Figure 1.10).

Figure 1.9 Kitchen utensils made of cork (Amorim, 2017).

Figure 1.10: Door handles make of cork (Amorim, 2017).

The chemical composition of this material consists of suberin (45%) which is the main component of the cell wall and the main responsible for its elasticity, lignin (22% insulation compound), polysaccharides (12% a cell wall compound that provides texture), tannins (6% supplies colour) and ceroid (5% and hydrophobic compound with assures the impermeability).

The cork cell is composed of suberin cells in the form of a tiny pentagonal or hexagonal prism and a complex fatty acid filled with an air-like gas, who take up 90% of the space. Commonly it has an average density of 200 kg/m^3 (Amorim, 2017).

According to the cellular structure of cork, one can define three main directions in relation to the trunk of the tree (Figure 1.11). The one that is aligned with the radius is designated as radial and the direction along the axis of the tree is called axial. Finally, the direction tangent to the surface of the tree is called tangential.

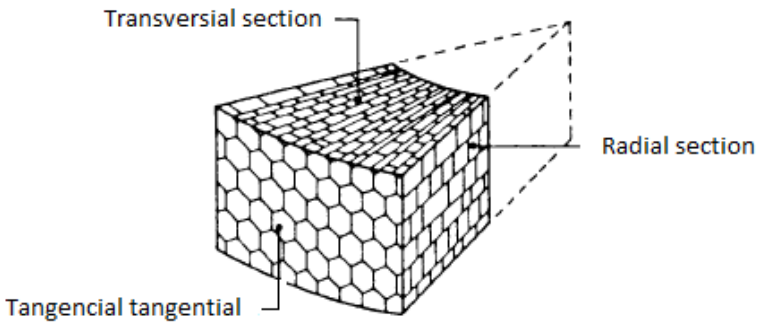

Figure 1.11: The three main directions of cellular structure of cork (Adapted from Silva et al. 2005).

1.3.2 The economic importance of cork in Portugal

In Portugal, with a bigger market than Porto wine, cork is considered as the most important national product of the primary sector (Gonçalves, 2000). During the year of 2016 this raw material hit all the records with 937,5 million of euros in exports. (Apcor, 2016)

Portugal appears at the forefront of this product, leading not only in the production but also in processing and trading. These results are the natural consequence of having the biggest area of cork tree dehesa in the world, that contains more than 730 thousands of hectares which means 34% of the total area and producing 100 thousand tons of cork (50% of total). It's also important to note that much of the world's harvest from other countries ends in Portugal with the purpose of processing. The human value is also very important to highlight, once in this regard, this industry is directly and indirectly responsible for 100 thousand jobs all over the world meanwhile in Portugal forestry has created 9000 jobs alone, but it is known that this number can be scale quickly if is taken into account the process (Apcor, 2015).

1.3.3 Industrial production of cork

The first step after collecting the barks is to pass them through water with the intention of relaxing the cork cell wall producing a straightening of the bent planks. After that the cork has to be boiled to win some flexibility before being worked. In this process the air that exists in the cells expand to configure a stretched uniform cell structure with an increase of its initial volume of 20%. Afterwards it is just a matter of checking if the colour, texture and thickness are regular, since these are characteristics that grant high quality (Thematking, 2005).

In companies like “Grupo Amorim”, the best planks, designed to the best cork stoppers, are fully natural and in order to be manipulated they are cut into strips with the help of a drill, taking out the future stopper with already a cylindrical shape (Figure 1.12). A qualified operator can drill over twenty thousand stoppers a day and the big advantage of doing this manually is that the worker can choose the best places of the strips. After this, the stoppers will still be mechanically verified by robots based on visual quality and all the remains (Amorim, 2015).

Figure 1.12: Stopper with a cylindrical shape.

1.3.4 Enhancing cork properties by addition of reinforcement materials

It is already well-known examples of reinforcement materials that were used to improve cork composites with remarkable results. In fact, as showed in the work of Fernandes et al. (2013) it was possible to increase in 27% the elastic modulus and 47% in the tensile strength by adding coconut fibre if compared with the unreinforced cork-based (50–50) wt.% composite.

Also in the work of Santos et al. (2017), carbon nanostructures were mixed with cork agglomerates but only clearly results were revealed in terms of fire retardancy.

1.4 Graphene based nanomaterials

Graphene is a rising star material which started to be investigated theoretically in Wallace (1947). Since then, and especially after being the main subject of the 2010 Physics Nobel prize, graphene is collecting attention not only from academics but also from industry. This material is the first two-dimensional atomic crystal produced artificially. The reason behind this popularity is connected with noble properties such as stiffness, strength, superior electrical (Cai et al. 2009) and thermal conductivity (5000 $Wm^{-1}K^{-1}$) and chemical tunability that arouse its potential for many applications. It counts with a theoretical specific surface area around 2630 m^2g^{-1} and with high intrinsic mobility (200 000 $cm^2s^{-1}\,v^{-1}$) as presented in this work about electron mobility in suspended graphene (Bolotin et al. 2008) and in this one about electron transport in graphene (Morozov et al. 2008). Graphene's Young's modulus is approximately 1TPa meanwhile its optical transmittance is nearly 1 (Zhu et al. 2010).

Graphene is nothing more than a form of carbon (Figure 1.13). This 2D-atomic crystal consists in a layer of sp^2 bonded carbon arranged in a hexagonal honeycomb lattice (Zhong et al. 2017).

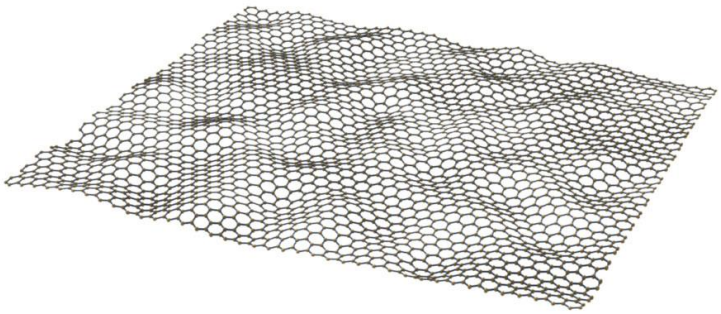

Figure 1.13: Graphene's sheet (Jameshedberg, 2015).

Graphene oxide (GO) composition is similar to a sheet of graphene decorated by oxygen and hydrogen and results from the exfoliation of graphite with oxidizers (Figure 1.14). Its popularity is justified due to the cost-effectiveness, the possibility of bulky scale production in trendy areas for GO like membranes, thin films or composites (Hummers and Offeman, 1958).

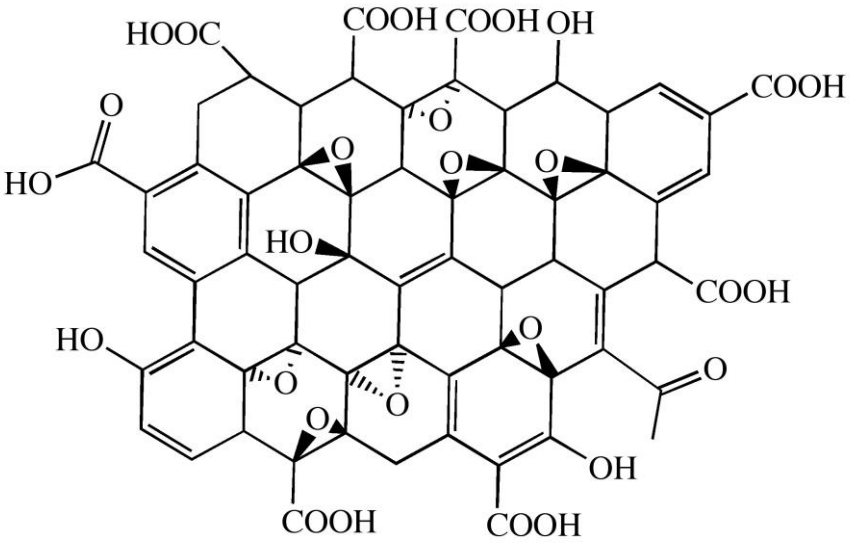

Figure 1.14: Graphene oxide structure (Greenoptimistic, 2017).

Graphite is a natural mineral mainly present in metamorphic rocks in Asia and America. Its popularity is principally obtained by the pencil lead, the central core of a pencil. Graphite is simply composed by multiple layers of graphene (Figure 1.15) [Substech, 2013].

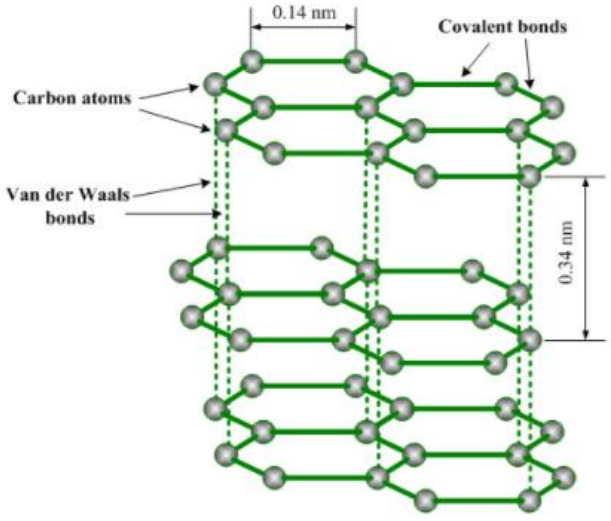

Figure 1.15: Graphite structure (Substech, 2017).

1.4.1 Graphene's mechanical properties – stiffness

Stiffness represents the rigidity of a certain material. It's the measure of the resistance offered by an elastic body to deformation. The value of graphene's stiffness is outstanding and relies on the stability of the overall hexagonal lattice. In a previous work, Lee et al. (2008) measured the elastic properties and intrinsic breaking strength of free-standing monolayer graphene membranes by nanoindentation in an atomic force microscope. In the following figure (1.16), it is clear graphene's performance is great when loaded.

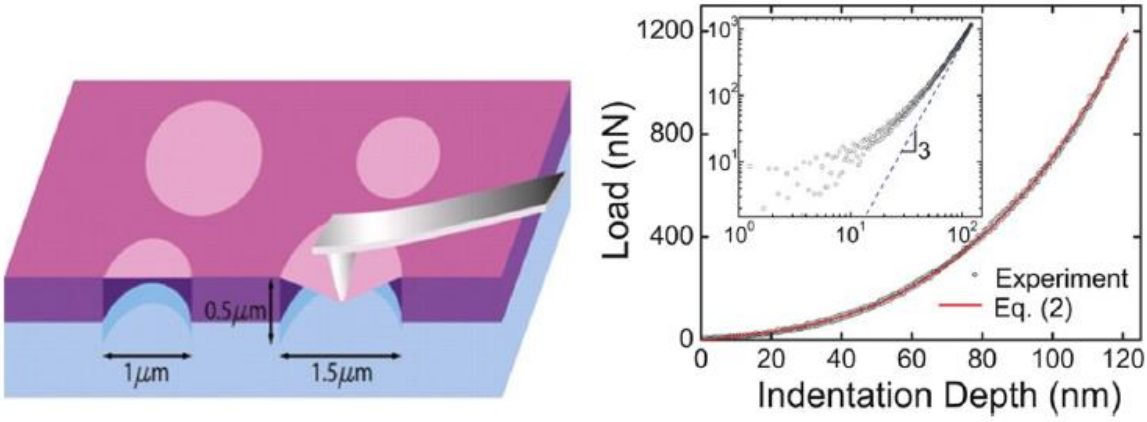

Figure 1.16: Nanoindentation setup in a suspended monolayer graphene membrane and the respective loading/unloading curve with increasing indentation depth (Lee et al. 2008).

1.4.2 Graphene's mechanical properties – strength

In engineering, the definition of strength is the ability to withstand an applied force without failure. The deformation caused is known as strain and it's common when analysing or characterizing a material to look at its stress-strain curve. In the fact, nobody was able to overcome C.Lee et al. (2008) results that placed the monolayer of graphene as the strongest material known. They registered the value of 42 Nm^{-1} to its intrinsic strength, which equivalent to 130 GPa. Qin et al. (2016) also dedicated time and used simulation to study the interlayer shear of mechanical properties of wrinkled multilayer graphene. In their conclusion, due to the geometrical locking effect the properties were expressively increased. An example of geometry of the graphene geometry absorbing a microbullet can be seen in figure 1.17.

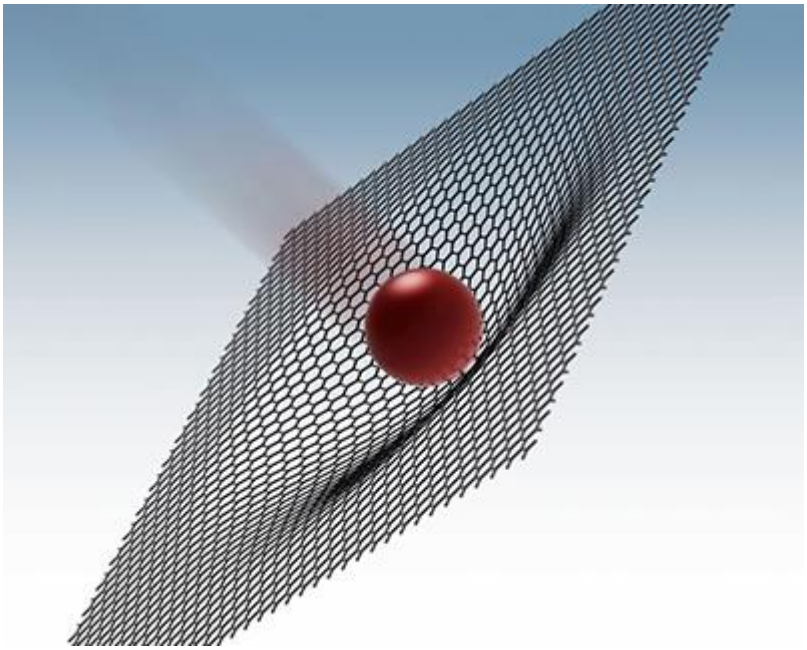

Figure 1.17: Simulation of graphene absorbing a microbullet (Physicsworld, 2014).

1.4.3 Graphene's mechanical properties – toughness

Another very important property in materials science is the toughness. This ability relies on the capability to absorb energy without fracturing. Graphene, as with other mechanical properties, shines in this one that plays between the concepts of strength and ductility. An interesting example was developed by Blees et al. (2015) when, fully inspired by kirigami techniques, they managed to manipulate the graphene's monolayer into springs in order to improve their initial stretched condition in 240% using a magnetic field (Figure 1.18). This work also suggests that the methods and the philosophy of Kirigami can be useful in areas like sensing, manipulation or nanoscale robotics.

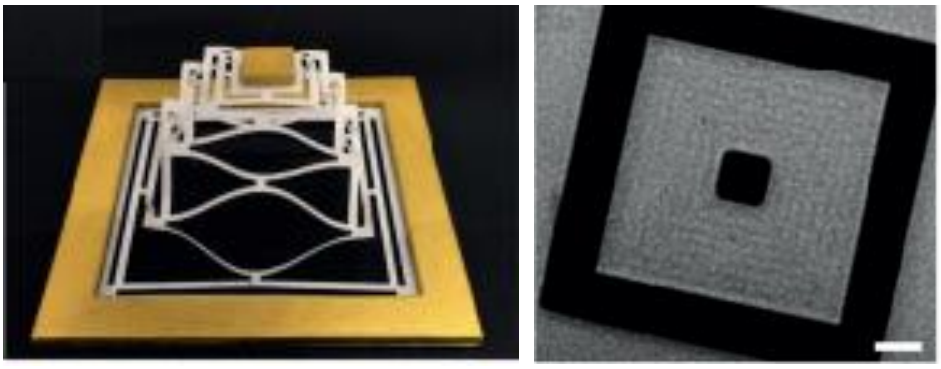

Figure 1.18: The Paper model (left) and graphene kirigami pyramid (right) (Blees et al. 2015).

1.4.4 Production of Graphene and Graphene Oxide

The biggest task to solve since the first moment that graphene was first isolated has been to associate a large scale of production with high quality of the final product. Actually, the use of graphene by many industries relies on these two parameters that not always are up to do it in the required way (Phiri et al. 2017). The methods that have been testified are mainly mechanical or chemical. Micromechanical cleavage was the first method to be tested successfully, being then associated to graphene's birth Geim and Novoselov (2004) found graphene using this technique, also known as "the scotch tape method". It can be executed without any sophisticated equipment and all it takes is a piece of adhesive tape placed onto then peeled off the surface of graphite. To get a single layer of graphene, an unstained tape is constrained against the graphite flakes adhering to the initial tape. Removing the two tapes cuts the graphite into smaller fragments. Although the high quality provided by this technique, the main issue these days is still industrialization of this process in a bulky scale. Another method to extract the "wonder material" from graphite is to exfoliate in different liquid media using ultrasound (Zhong, 2015). Since it is known that the van der Waals bonds (which are weak compared with covalent bonds that are link the carbon atoms in graphene) hold the layers of graphene collected forming graphite, the liquid phase exfoliation (LPE) operates directly there, overcoming the van der Waals forces bonds. Although LPE has potential in scaling, it faces other kind of problems such as very limited dispersity of the graphene that acts as an unsociable macromolecule. Additionally, the dispersing solvents are not only very expensive but also have either high boiling point or are corrosive (Zhong, 2015). Obtaining graphene via graphite oxide is another procedure that comprises the exfoliation of graphite in an oxidant medium. This process promotes the breakage of the van der Waals bonds introducing oxygen groups on the surface of exfoliated graphite sheet, which helps their diffusion in water. Then graphite oxide goes to a procedure of sonication that finishes with dispersed graphene oxide sheets in water. In order to reach graphene, it's required to pass through a process of reduction. The work of Dimiev and Tour (2014) is a model example of what was described. Electrochemical exfoliation can be an option too, as related by Parvez et al (2014). In this case, there is an interaction between oxidation and reduction at the anode and cathode with an organic electrolyte. It is applied positive current at the electrodes (graphite and platinum) which will provoke oxidation and consequently the ions that are negatively charged from the electrolyte will be intercalated into graphite layers (Figure 1.19).

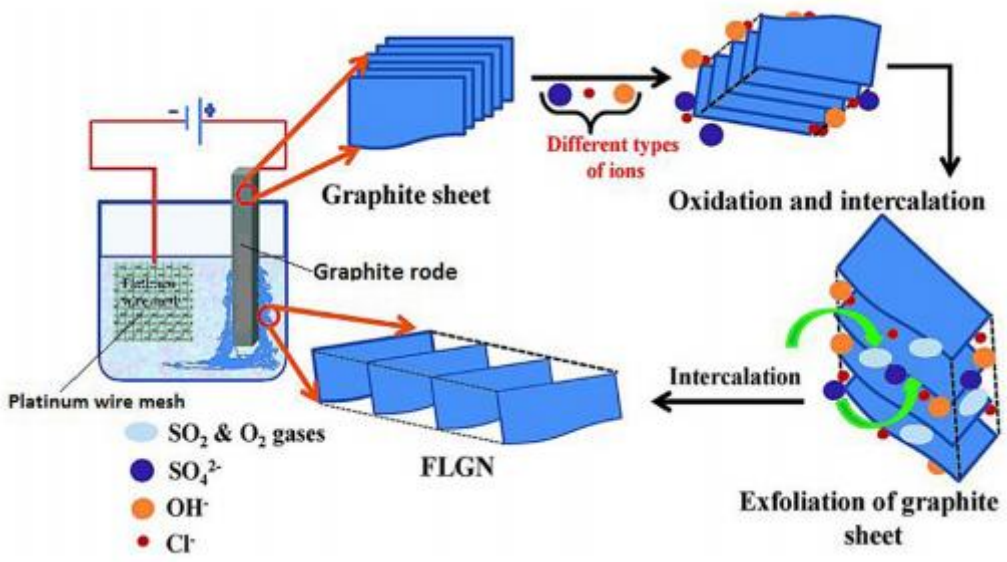

Figure 1.19: Schematic diagram of the mechanism of electrochemical exfoliation of graphite. The electrodes used were graphite rode and platinum wire mesh for the anode and cathode, respectively (Parvez et al. 2014).

Polymers based in nanocomposites are attracting general interest, specifically once it was documented and established that exfoliated clays could improve substantially the mechanical component of polymers (Kojima et al. 1993; Okada et al. 1988; Kawasumi 2004). The enhancements reached by these nanohybrid materials can not be achieved by conventional composites (Kuilla 2010). A nanocomposite is a material where at least one of its components is nano-sized, the nanocomponents added to improve the properties of the original material (Okpala 2013). Apart from that, the increase knowledge of the dispersion of graphene carried this specific sector to the limelight. That being said, improvements are tangible at a low filler loading. Graphite, graphene and graphene oxide give distinct possibilities of approach in order to be used to improve the physicochemical characteristics of a composite. Studies have been reported on expanded and exfoliated graphite composites based on several polymers such as epoxy (Yasmin et al. 2006; Debelak et al. 2007), PMMA (Zheng and Wong 2003; Ramanathan et al. 2007), polypropylene (PP) (Kalaitzidou et al. 2007; Wakabayashi et al. 2008), LLDPE (Kim et al. 2009; Kim and Drzal 2010), HDPE (Zheng et al. 2004), Polystyrene (PPS) (Zhao et al. 2007), Poly(vinyl alcohol) (PVA) (Liang et al. 2009; Zhao et al 2010), Thermoplastic Polyurethane (TPU, Lee et al. 2009; Liang et al. 2009), phenylethynyl-terminated polyimide (PETI, Du et al. 2004) and silicone rubber (Cho et al. 2005). Table 1 summarizes the data of the percentage of improvement relative to mechanical properties comparing the nanocomposites with graphite or graphene versus the unreinforced ones.

Table 1: Examples of mechanical properties of graphene/graphite-based polymer nanocomposites documented. Adapted from T. Kuilla et al. (2010).

Matrix	Filler type	Filler loading (wt.%a, vol.%b)	Process	Increase E	Increase TS	Increase FS	Reference
Epoxy	EG	1[a]	Sonification	8%	-20%		Yasmin et al. 2006
	EG	1[a]	Shear	11%	-7%		
	EG	1[a]	Sonification and shear	15%	-6%		Yasmin et al. 2006
	EG	0.1[a]	Solution			87%	Yasmin et al.2006
							Debelak et al. 2007
PMMA	EG	21[a]	Solution	21%			Zheng and Wong 2003
	GNP	5[a]	Solution	133%			(Ramanathan et al. 2007
PP	EG	3[b]	Melt	100%	4%		Kalaitzidou et al. 2007
	xGnP-1	3[b]	Melt	33%			Kalaitzidou et al. 2007
	xGnP-15	3[b]	Melt			-20%	Kalaitzidou et al. 2007
	Graphite	2.5[b]	Melt			-33%	(Wakabayashi et. Al 2008
LLDPE	xGnP	15[a]	Solution		200%		Kim et al. 2009
	Parrafin coated xGnP	30	Solution		22%		Kim and Drzal 2010
HDPE	EG	3[a]	Melt	100%	4%		Zheng et al. 2004
	UG	3[a]	Melt	33%			Zheng et al. 2004
PPS	EG	4[a]	Melt			-20%	Zhao et al. 2007
	S-EG	4[a]	Melt			-33%	Zhao et al. 2007
PVA	GO	0,7[a]	Solution		76%		Liang et al. 2009
	Graphene	1,8[b]	Solution		150%		Zhao et al. 2010
TPU	Graphene	5,1[b]	Solution	200%			Lee et al. 2009

	Sulfonated Graphene	1[a]	Solution		75%		Liang et al. 2009
PETI	EG	5[a] 10[a]	*In situ* *In situ*	39% 42%			Du et al. 2004 Cho et al. 2005

Note (Abbreviations): E- elastic modulus; TS- tensile strength; FS- flexural strength.

A key point to build an effective composite is linked to the dispersion of the nanomaterial into the host matrix and many studies contemplate that (Texter 2014; Konios 2014; Giudice 2017). With a view to manufacturing industry, few topics should be take into account such as increasing the range of dispersing solvents (preferentially embracing the less toxic and volatile), enhance dispersion stability in terms of concentration, time and temperature and safe handling. All these facts correspond to challenges that belong to the present, having an effective homogeneity as a must. In fact, dispersion of graphene in polymers represents a difficult answer. This can be done by either diffusing the graphene into a co-solvent with the polymer, or diffusing graphene in a monomer and polymerising in situ to produce a composite (Johnson 2015). Young et al. (2011) mixed a single graphene atomic layer with a two layers polymer of poly(methyl methacrylate) beam involving with it and they discovered that the distribution of strain across the graphene was uniform until the levels of matrix strain reached 0.6% but the same did not happen above that value (Figure 1.20). This variation in the strain was verified due to a fragmentation process that develop of cracks in the polymer coating layers caused by a poor level of adhesion between the graphene and polymer layers.

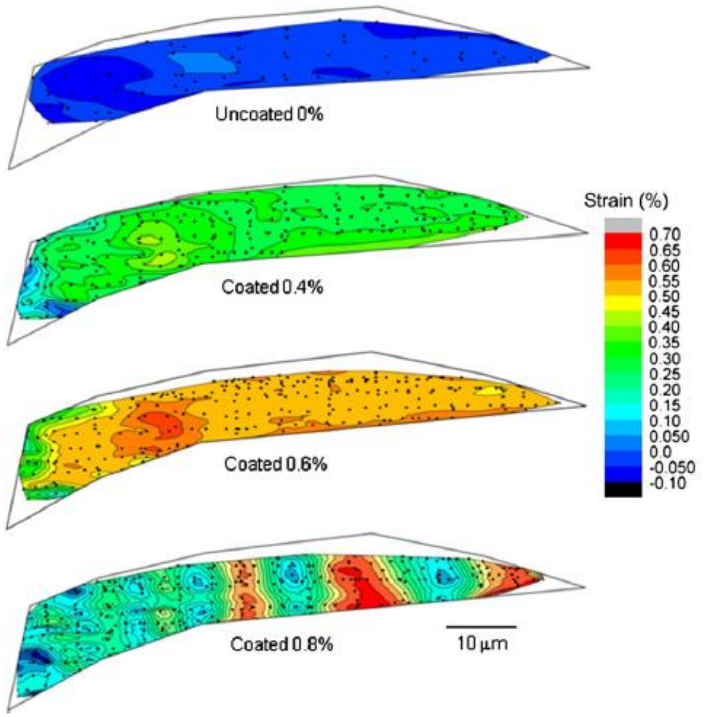

Figure 1.20: Simulation of the distribution of strain in different percentages of graphene coating (Young et al. 2011).

1.5 Bio-based polymers

"…Europe must move to an economy that is no longer dependent on oil, we must drive the transition from a fossil-based to a bio based society with research and innovation as an engine. It is good for the environment, food and energy security and for Europe's future…"

EU commissioner for Research, Innovation and Science Máire Geoghegan-Quinn

Polymers are in our world everywhere not only derived by the products that we decide to use but also in nature. Their popularity is undeniable, specially the synthetic ones, mostly used in industry. Besides that, there are also natural polymers that exist in living beings in the shape of proteins, carbohydrates (such as starch, glycogen or cellulose) and nucleic acids (Baird et al. 2014). In terms of their physical response to heating they can be divided in two main groups: i) Thermoplastics that once heated can modify their outline and be manageable above a specific temperature, returning to the initial form when the temperature goes down. These ones are generally easier to be processed, easier to be recycled and for that reason more environmental-friendly. ii) Thermosets also get smoother when heated and can be moulded but the main difference is that they harden permanently

after cooled down. Despite these drawbacks thermosets commonly perform better when is required high heat resistance or even when their mechanical properties are involved.

The plastics sector symbolizes the main application for polymers in our present, having exploded world widely in 1950 (Storz and Vorlop, 2013), reaching a production level of 322 million ton in 2015, being connected to over 1.5 million jobs nowadays (MacArthur, E. 2016). The ones that are more required are synthetized from petroleum, specifically, polyethylene (PE), polypropylene (PP), polystyrene (PS) and poly(ethyleneterephtalate) (PET). As it is understandable by these numbers, it has been created a dangerous connection that drove humanity to be dependent of something that is limited.

As previously said, most of these polymers are hard to be recycled, so it would not solve anything if recycling acts alone. Henry Ford said once that, in order to reduce the fuel consumption in cars, industry should put effort on producing lightweight cars, investing in new materials. In this scenario, a similar solution can occur to inverter this negative and limited trend which is to shift from petroleum-based polymers to bio-based ones (Jeon et al. 2013).

Bio-based polymers are the definition for all the materials that are originated from renewable resources. The interest in bio-based polymers has grew up exponentially in recent years due to the craving for dependency of fossil fuels. The first wave of bio-based polymers was targeted to obtain polymers from agricultural feedstock such as potatoes and corns (starch, cellulose, alginates). After that and thanks to the developments in biotechnology, it was possible to produce polymers close to the popular ones by synthetically constructing monomers from renewable resources as lignocelluloses (starch and cellulose), fatty acids and organic waste using bacterial fermentation, giving rise to PBS, PE, PLA and so on Figure 1.21 (Babu et al. 2013).

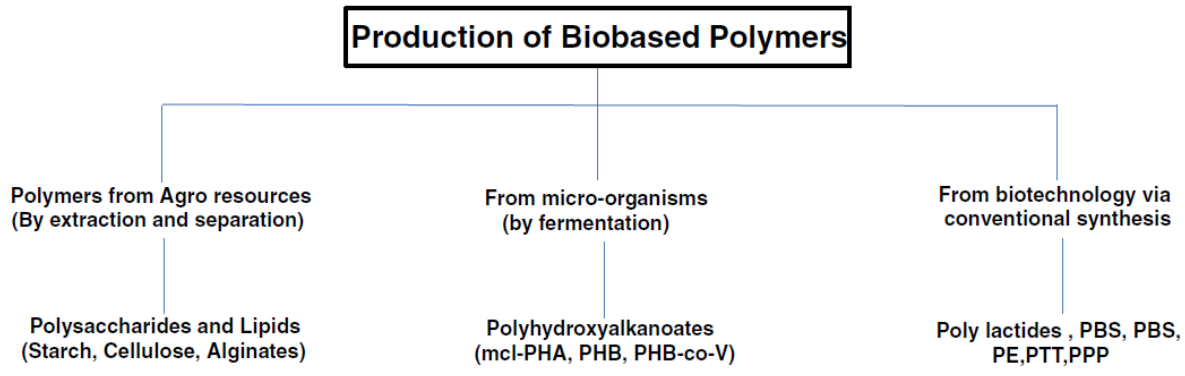

Figure 1.21: Bio-based polymers production variants (Luc and Eric, 2012).

A market study made in 2013 (Mirabal et al. 2013) predicted the production of bio-based polymers will triple from 2011 to 2020 reaching a maximum of 12 million tonnes. The most notable variation is seen in bio-based PET. The second one belongs to polymers who are chemically very close to their petrochemical "brothers" such as PE, PP. Finally even PLA and PHA will almost quintuple their capacity until 2020 (Figure 1.22 and Figure 1.23).

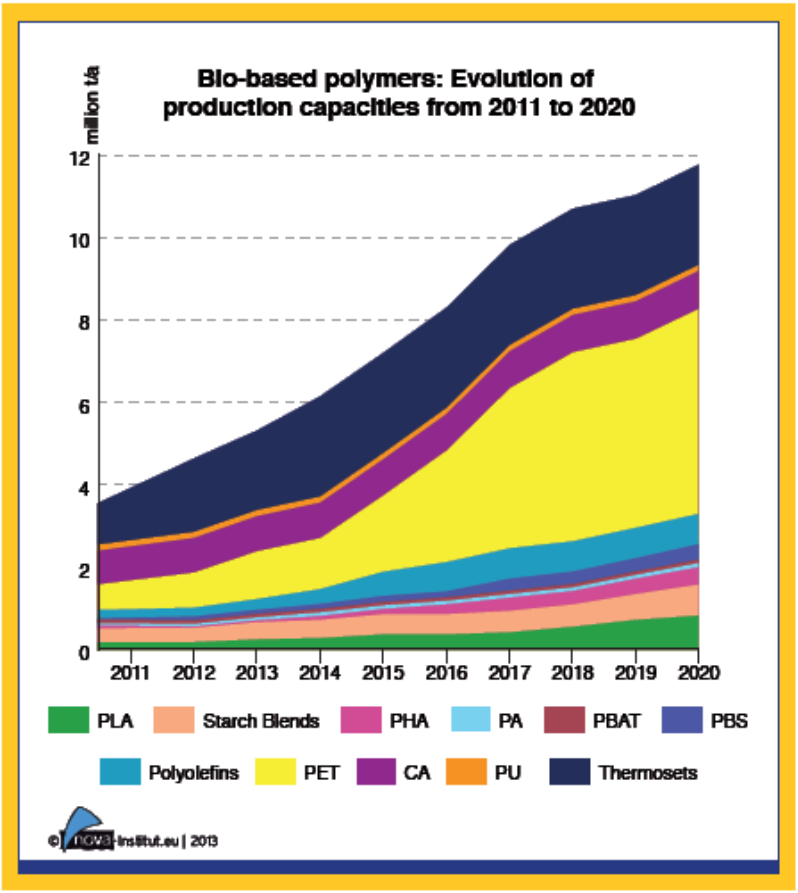

Figure 1.22: Prediction of the evolution of bio-based polymers' production from 2011 to 2020 (Mirabal et al. 2013).

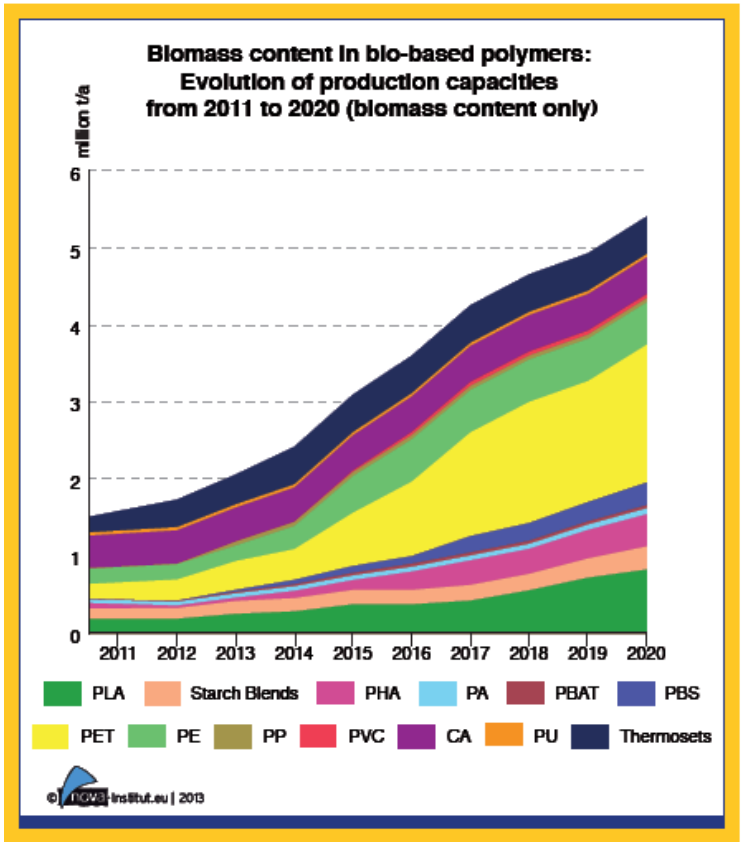

Figure 1.23: Prediction of the evolution of bio-based polymers' (biomass only) production from 2011 to 2020 (Mirabal et al. 2013).

1.5.1 Natural bio-based polymers

Polylactic acid (PLA) has a basic constitutional unit, lactic acid, and belongs to the family of aliphatic polyesters. It has been commercialized from the beginnings of 1990 although it is known for 150 years (Rabu et al. 2013). PLA is versatile in terms of processing conditions, has a high rigidity and good transparency. The downside stands to its high cost and poor mechanical ductility. The applications of PLA are numerous and mainly dedicated to the hospital area as one can see in the following table.

Table 2: Application of PLA and their blends in various fields (adapted from Rabu et al. 2013).

Polymer	Applications	Reference
PLGA/PGA	Ovine pulmonary valve replacement	Williams et al. 2009; Sodiar et al. 1999; Cheng et al. 2009

PLA/chitosan PLA/PLGA/ chitosan PLA	Drug carrier/drug release	Jeevitha and Kanchana 2013; Javanth and Vinod 2012; Nagarwal et al. 2010; Chandy et al 2000; Valantin et al. 2003
PLGA and copolymers	Degradable sutures	Rajev 2000
PLA/HA composites	Porous scaffolds for cellular applications	Jung-Ju et al. 2012
PLA-CaP and PLGA-CaP	Bone fixation devices, plates, pins, screws, and wires, orthopaedic applications	Huan et al. 2012
PDLLA	Coatings on metal implants	Schmidmaier et al. 2001
PLA/PLGA	Use in cell-based gene therapy for cardiovascular diseases, muscle tissues, bone and cartilage regeneration, and other treatments of cardiovascular and neurological conditions	Coutu et al. 2009; Kellomaki et al. 2000; Papenburg et al. 2009;
PLA and PLA blends	Packaging films, commodity containers, electrical appliances, mobile phone housings, floor mats, automotive spare parts	Auras et al. 2010
PLA	Textile applications	Gupta et al. 2007; Avinc and Akbar 2009

Polyhydroxyalkanoate (PHA) also belong to the family of polyesters with the singularity of being produced by bacterial fermentation. It is chemically defined as linear aliphatic polyester and thanks to its ability to be melted and shaped they can be used directly as plastics without adjustments. The applications for this bio-based polymer are principally relative to cosmetics and medical areas (Voevodina and Kržan, 2013).

Table 3: Application of PHAs and their blends in various fields (adapted from Rabu et al. 2013).

Polymer	Applications	Reference
P(3HB), P(3HB-co-3HHX) and blends	Scaffolds, nerve regeneration, soft tissue, artificial oesophagus, drug delivery, skin regeneration, food additive	Yang et al. 2002; Chen et al. 2005; Bavram and Denbas 2008; Tang et al. 2008; Clarinval and Halleux 2005
mcl-PHA/scl-PHA	Cardiac tissue engineering, drug delivery, cosmetics, drug molecules	Sodian et al. 2000; Wang et al. 2003; de Roo et al. 2002; Zhao et al. 2003; Ruth et al 2007

P(4HB) and P(3HO)	Heart valve scaffolds, food additive	Valappil et al. 2006; Türesin et al. 2001
P(3HB-co-4HB), P(3HB-co-3HV)	Drug delivery, scaffolds, artificial heart values, patches to repair gastrointestinal tracts, sutures	Williams et al. 1999; Chen et al. 2008; Freier et al. 2002; Kunze et al. 2006; Volova et al. 2003; Philip et al. 2007
PHB, Mirel P103	Commodity applications, shampoo and cosmetic bottles, cups and food containers	Amass et al. 1998; Walle et al. 2001

Polybutylene succinate (PBS) is also an aliphatic polyester with good tensile and impact strength but with poor mechanical flexibility that limits the range of its applications. PBS is commercially attractive in areas that involve packaging, hygiene products and others as it's possible to check in Table 4

Table 4: Application of PBS and their blends in various fields (adapted from Rabu et al. 2013).

Polymer	Applications	Reference
PBS/PLA blend	Packaging films, dishware, fibers, medical materials	Weraporn et al. 2011; Liu et al. 2009; Bhatia et al. 2007; Lee et al. 2006
PBS and blends	Drug encapsulation systems	Cornelia et al. 2011
PBS/starch	Barrier films	Jian-Bing et al. 2011
PBS and copolymers	Industrial applications	Jun et al. 2010
PBS ionomers	Orthopedic applications	Jung et al. 2009

Bio-polyethylene. (Bio-PE) is chemically similar to the most common version of PE (the fossil-based one), has the same technical properties and it is not biodegradable. Since PE and their variants are the most produced plastics in the world it is imperative to competently produced the bio version. Nowadays Bio-PE manufacturing is based in 3 stages. The first one is the ethanol synthesis by fermentation from sugar. Then it's necessary to occur chemical dehydration to transform ethanol in ethylene and finally it passes through a reaction of polymerisation giving rise to polyethylene (PE)

[94]. Bio-PE can replace PE in all applications, many of them are already documented as described in Table 5.

Table 5: Application of Bio-PE and their blends in various fields (adapted from Rabu et al. 2013).

Polymer	Applications	Reference
Bio-PE	Plastics bags, milk and water bottles, food packaging films, toys	Vona et al. 1965
Bio-PE and blends	Agricultural mulch films	Kasirajan and Ngouaji 2012

Bio-PET can be obtained from the monomers ethylene glycol and terephthalic acid using bio-based ethylene glycol. It's globally used in food, textiles, foils and fibres industry. In 2015, Coca-Cola revealed to the world a 100% bio-based PET bottle in World Expo in Milan (Figure 1.24).

Figure 1.24: Bottle 100% bio based pet exposed by Coca-Cola in World Expo in Milan (Greenchemicalsblog, 2015).

Starch is a unique bio-based polymer produced by green plants for energy storage in structures known as starch granules, located in plant cells. Starch, the final result of plants' photosynthesis, is used as a thermoplastic polymer in packing, fishing bait bags and films.

Table 6: Application of Starch and their blends in various fields (adapted from "Current progress on bio-based polymers and their future trends")

Polymer	Applications	Reference
Starch	Orthopaedic implant devices as bone fillers	Ashammakhi and Rokkanen 1997;
Starch/ethylene vinyl alcohol/HA starch/polycaprolactone blends	Bone replacement/fixation implants, orthopaedic applications	Mainil et al. 1997; Mendes et al. 2001; Marques and Reis 2005
Starch/cellulose acetate blends with methylmethacrylate and acrylic acid	Bone cements	Espigares et al. 2002
Modified starch	Food applications	Jaspreet et al. 2007; Fuentes et al. 2010
Starch derivatives	Drug delivery	Asha and Martins 2012
Thermoplastic starch	Packaging, containers, mulch films, textile sizing agents, adhesives	Zhao et al. 2008; Maurizio et al. 2005; Ozdemir and Floros 2004; Dave et al. 1999; Guo et al. 2005; Kumbar et al. 2001; Li et al. 2011

Cellulose, the main component of plants' cell wall, is a crystalline polysaccharide. Its structure is very similar to the starch, diverging only where glucose units are linked. The production of cellulose resorts mainly on cotton fibers and wood. In terms of mechanical properties, cellulose has a high tensile strength that goes from 62 up to 500 MPa, depending, as it usual in these polymers, on the specific blend composition (Rabu et al. 2013)

Table 7: Application of Cellulose and their blends in various fields (adapted from Rabu et al. 2013).

Polymer	Applications	Reference
Cellulose esters	Membranes for separation	Kumano and Fujiwara 2008
Carboxylated methyl cellulose	Drug formulations, as binder for drugs, film-coating agent for drugs, ointment base	Chambin et al. 2004; Obae et al. 1999; Westermark et

		al. 1999; Hirosawa et al. 2000
Cellulose acetate fibers	Wound dressings	Orawan et al. 2008; Abdelrahman and Newton 2011
Hydroxyethyl cellulose	Spray for clothes polluted with pollen	Hori et al. 2005
Modified celluloses, cellulose whiskers, microfibrous cellulose	Barrier films, water preservation in food packing	Amit and Ragauskas 2009
Cellulose nanofibers	Textile applications	Zeeshan et al. 2013
Cellulose particles	Chromatographic applications, chiral separations	Levison 1993; Arshady 1991

Collagen is the most abundant protein in the animal world with more than 27 variations of itself. It's a well-known biomaterial used in many cosmetics thanks to its biocompatibility and biodegradability. In engineering, taking advantage of its stretching abilities, it's used in skin replacement and other biomedical applications (Lee et al. 2001) and in food industry (Gomez-Guille et al. 2011).

Chapter 2
Materials and methods

2.1 Materials

The cork grains used in the experimental campaign were provided by Amorim Cork Composites (ACC) already from previous studies, namely Santos et al. (2017). Two different particle sizes were employed throughout this work: 0.5-1mm and 2-4mm, which from now on will be reported as small and large grains, respectively. An illustrative example can be seen next (Figure 2.1).

Small Grain (0.5 to 1mm)	Large Grain (3 to 4mm)
	

Figure 2.1: Small and large cork grains.

One of the binders used was supplied by Flexpur (Ovar, Portugal), and denominated as flexible (Figure 2.2) due to its chemical and physical features. This designation, although poor, was the only information provided by Flexpur and it is based on the comparison between other binders produced by the company. In any case, this company is known for the production of polyurethane (PU) pre-polymers based products. The production of polyurethane is normally related by reacting a di- or polyisocyanete with a polyol. It was also mention by Flexpur that the binder is based on most common used isocyanates, which are the aromatic diisocyanates, toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). In their work, Santos et al. (2017) also used these binders in the preparation of cork agglomerates. The authors investigated the chemical composition of the binders using a Fourier Transform Infrared Spectroscopy - Attenuated Total Reflectance, (FTIR-

ATR) analysis, and the results indicated that, most probably, the flexible binder is a PU pre-polymers based TDI.

Figure 2.2 PU TDI based binder used in the work.

The bio-binder used (Figure 2.3) in the other experimental campaign was supplied by the Resiquímica – Resinas Químicas, S.A. and belongs to a selection of products denominated ERIS (Eco and Renewable Integrated Solutions). Their compounds are not harmful to nature or to human health and there is a strong motivation to maximize renewable sources in the constituents used. The binder used, ERIS 140, is an unsaturated polyester resin with 54% of renewable raw materials. (Other information concerning ERIS 140 is available in the technical data sheet, present in the annexes section.)

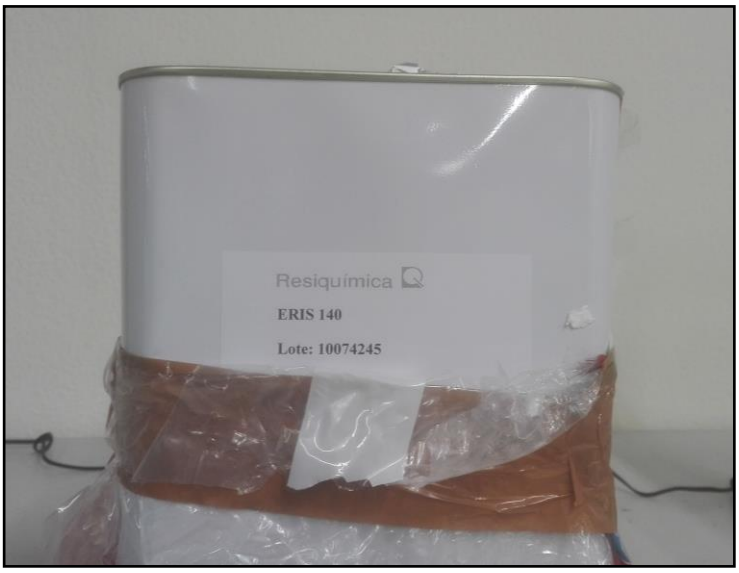

Figure 2.3: Biobased synthetic binder used in this work.

The graphene nanoplates (GNP) powder was provided by Cheap Tubes Inc (USA) and used as given (Figure 2.4), and graphene oxide (GO) (4mg/mL aqueous dispersion) was purchased from Graphenea (Spain). GO was dried by lyophilization and then submitted to a ball milling process in order to obtain small sized particles (Figure 2.5) and gather a more uniform dispersion in the final composite. All other information can be accessed in the data sheets provided in the end.

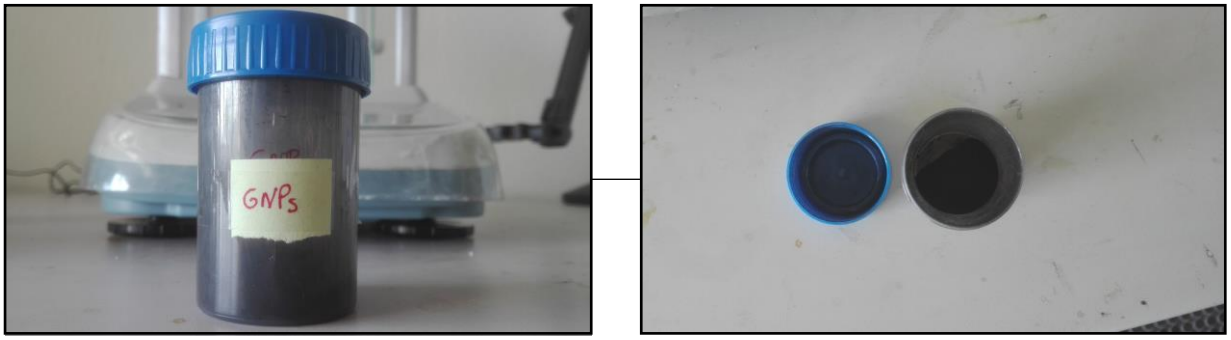

Figure 2.4: GNP used in the present work.

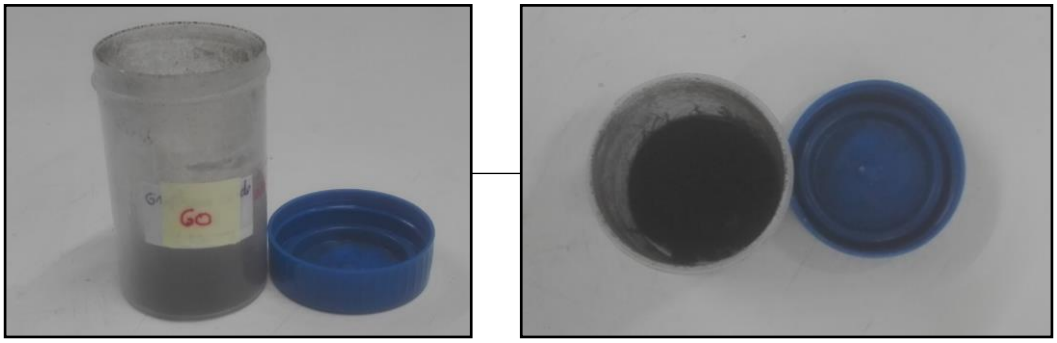

Figure 2.5: GO used in the present work.

2.2 Sample production

2.2.1 Graphene and oxide graphene nanocomposites

The production of samples consisted in four main steps. First it was weighted the amount of constituents needed to the final composite in an analytical balance (Figure 2.7). Next, the GNP and GO were mingled to the agglomerated cork in plastic bottles and submitted to vigorous mixing for 3 hours (Figure 2.6).

Figure 2.7: Balance used.

Figure 2.6: Mechanical stirrer used.

Then it was added water to the cork part, meanwhile an electric mixer (Figure 2.8) was homogenizing the blend. After 1 minute, the binder was introduced even though the mixer would only stop 5 minutes afterwards. Finally, it was compressed in a press machine until achieving the desired density and heated to 140ºC for two hours in the oven (Figure 2.9), assuring the cure of the polymer in the mould (Figure 2.10).

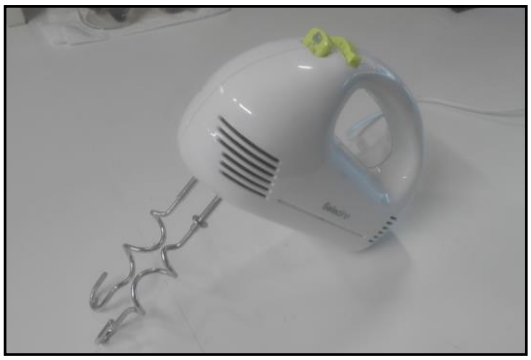

Figure 2.8: Electrical mixer used.

Figure 2.9: Oven used.

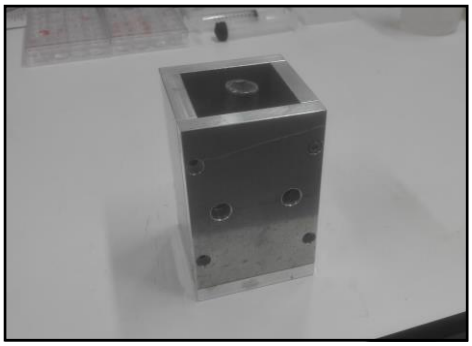

Figure 2.10: Mould used.

Table 8: Design of experiments for the preparation of cork composites with GNP and GO.

Binder type	**Binder (wt.%)**	**Density(kg/m^3)**	**Grain Size**	**Reinforcement (wt.%)**
PU TDI based	10	160	Small(0.5-1mm)	0.1 (GPN)
PU TDI based	10	160	Small(0.5-1mm)	0.5 (GPN)
PU TDI based	10	160	Small(0.5-1mm)	1 (GPN)
PU TDI based	10	160	Small(0.5-1mm)	0.1 (GO)
PU TDI based	10	160	Small(0.5-1mm)	0.5 (GO)
PU TDI based	10	160	Small(0.5-1mm)	1 (GO)
PU TDI based	10	160	Small(0.5-1mm)	0 (Control test)

2.2.2 Bio-polymer samples

The methodology adopted in this section was very similar to the last described. The main difference relies in the curing process of the binder used in the procedure. While in the of PU pre-polymer binder, the curing process is achieved by the presence of water and high temperatures, the bio-based binder curing involves the presence of an initiator, accelerator and high temperature. A pre-mixture of the bio-binder ERIS 140 with the chemical initiator (2-butanone peroxide) as well as a chemical accelerator (cobalt (II) 2-ethylhexanoate solution) (Figure 2.11) were added to the cork and mixed for 30 seconds. The concentration of chemical initiator and accelerator used were 2 wt. % and 0.4 wt. %, respectively, with respect to the binder. Then the mixture was poured in the mould, pressed and heated for 140ºC, for 2 hours.

Figure 2.11: Chemical accelerator and initiator.

Table 9: Design of experiments with bio-based polymer

Binder type	**Binder (wt.%)**	**Density(kg/m^3)**	**Grain Size**
Bio (ERIS 140)	20	160	Small(0.5-1mm)
Bio (ERIS 140)	20	160	Large(2-4mm)

The amount of binder wt. % will be justified in the results section.

Chapter 3

Experimental Campaign

In this work, it was intended to study two main factors in cork agglomerates production. First, the influence of GNP and GO as reinforcement in cork agglomerates using a synthetic PU pre-polymer binder. Secondly, investigate the viability of using a bio-based polyester binder to agglomerate cork granulated materials.

In order to validate both variations of this upgraded agglomerated cork, one with a bio-polymer resin and other one with the reinforcement of GNP and GO, quasi-static compression tests were performed. Variables such as the percentage of the graphene, bio-binder or the grain size used were also explored to pursuit an optimal solution for the composite in question.

The goal of this work focuses primarily practical questions with high chances of being implemented in the real world, or to somehow contribute to the growth of analogue solutions. With this in mind, the mechanical properties were analysed from different angles like the energy density, the plateau-stress, and the strain densification.

To consolidate the argument and to ensure repeatability, every test showed was repeated at least 3 times for each case.

Figures 3.5, 3.7 and 3.9 present the stress-strain curve for the considered cases. Since the samples that were analysed correspond to cellular materials, the mechanical response of the tests was the one expected. At the elastic stage, for a small amount of strain corresponded a slight increase of stress. After that, occurs the so-called plateau stress, in which, for an almost constant applied stress, there is a deformation that goes from 5 to 75%, depending on the specific characteristics examined. This capability is precisely why cellular materials are the key in applications where a stable absorption of the energy is required. Posteriorly, the samples reach densification, known for a huge increase of stress for a small strain increment.

To achieve the quasi-static compression tests it was used a Shimadzu AG50 KN universal test machine. The samples, with 25x25x25 mm, were placed in the center (Figure 3.1) and compressed at a slow strain-rate (0,4 mm/min). The result of the given curves permitted to handle the output in order to have access to the stress-strain curve, and consequently the energy absorbed per volume.

Figure 3.1: Uniaxial quasi-static compression test.

3.1 Bio-polymer

As mentioned before, bio-based biomaterials are a trend that gained popularity by being a necessity of nowadays. Therefore, there are not many documents reporting the use of a bio binder in the preparation of agglomerated cork. As the result, it was hard to predict anything.

Initially, in this dissertation, it was tried to make the composite with the small grain (1-2mm) and 10 wt. % of the binder since it is the percentage used, not only to follow the parameters of the nanocomposites with graphene, but also to add value to what was done in Santos et al. (2017) work, keeping those conditions equal. Nevertheless, once the sample started to be compressed, it collapsed almost immediately, not being possible to get any values to report (Figure 3.2).

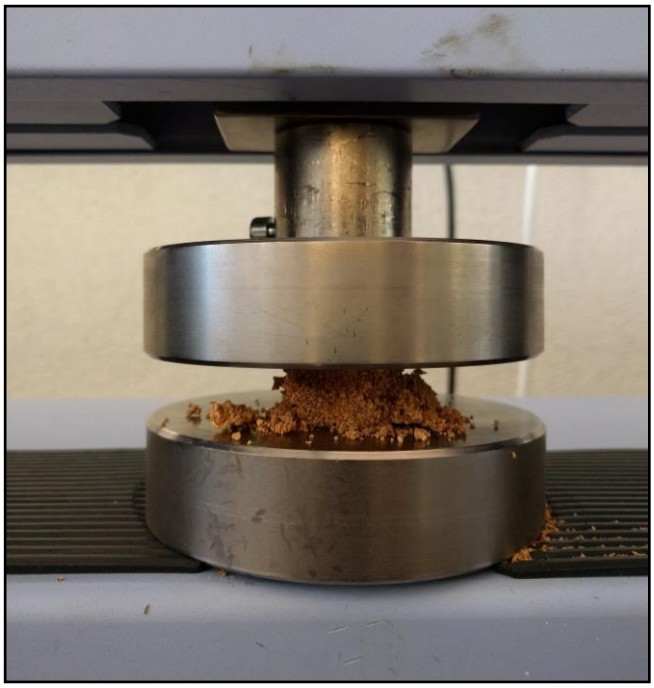

Figure 3.2: Disintegration of a sample with 10 wt. % of bio binder in the start of the compression test.

The same happened with a composition of 15 wt. % of bio-binder, as it is possible to be seen in figure 3.3, whereby it was tried 20% (figure 3.4) with success (at least as far as its integrity is concerned).

Figure 3.3: Sample with 15 wt. % of bio binder after a compression test attempt.

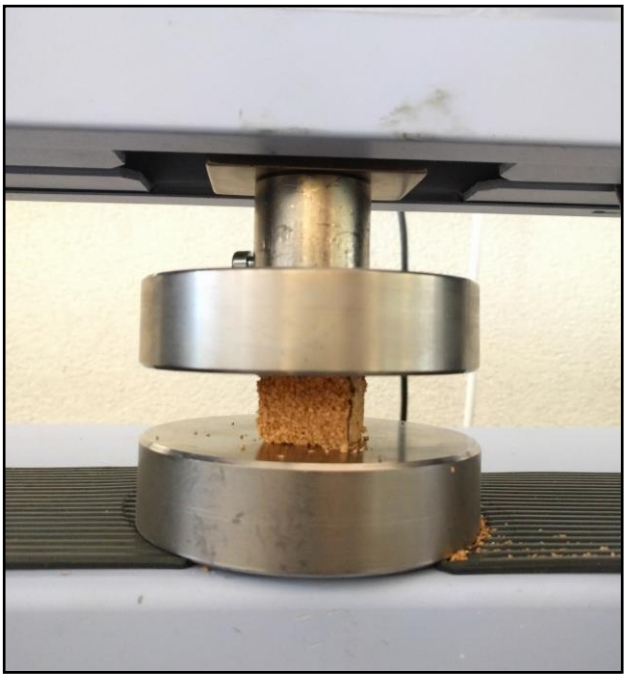

Figure 3.4: Sample with 20 wt. % of bio binder during a uniaxial compression test.

To test and describe the mechanical response of this resin, as well as to compare with a larger grain, several samples were prepared with the same density (160kg/m^3) and using the same methodology that was previously described.

When comparing the results of bio resins with the synthetic one, it is possible to deduce that the difference between its Young's modulus is non-existent. However, it is precisely afterwards that the main discrepancy occurs. The plateau stress of the bio binder sample is less pronounced. That is, for a certain value of strain, it corresponds lower stress, which implies considerably less energy absorbed. In the matter of densification stage, the non-bio resin takes place slightly primarily, around 65% in terms of strain, against 75% from bio-composite. Accordingly with what was described by Santos et al. (2017), the most probable reason for that, is that the bio binder corresponds to a more flexible binder than the non-bio one.

It is likely that the behaviour of the sample subjected to a quasi-static compression test relies on the resin used, being that directly related to the properties of the final cork agglomerate.

When comparing the influence of the grain size used, some notes are possible to be taken. In spite of the similar characteristics until the middle of the total strain (around 50%), the larger grain overcomes, in what regards to the mechanical properties, the small one. A higher plateau, for a longer period of strain, makes grains with 2 to 4 mm better energy absorber. This fact can be justified due

to the lack of preponderance of the binder. Since the cork grains are larger, the bio agent has a less important role.

Probably the concentrations of the initiator and accelerator are not the most suitable for this procedure, since it was observed that after mixing, all the components (binder, initiator and accelerator) the mixture turns suddenly to a gel. This make that the mixing process of the binder mixture with granulated cork need to be very fast (only 30 seconds) and a poor mixing process was obtained. The concentrations of initiator and accelerator needed to be optimized in the future.

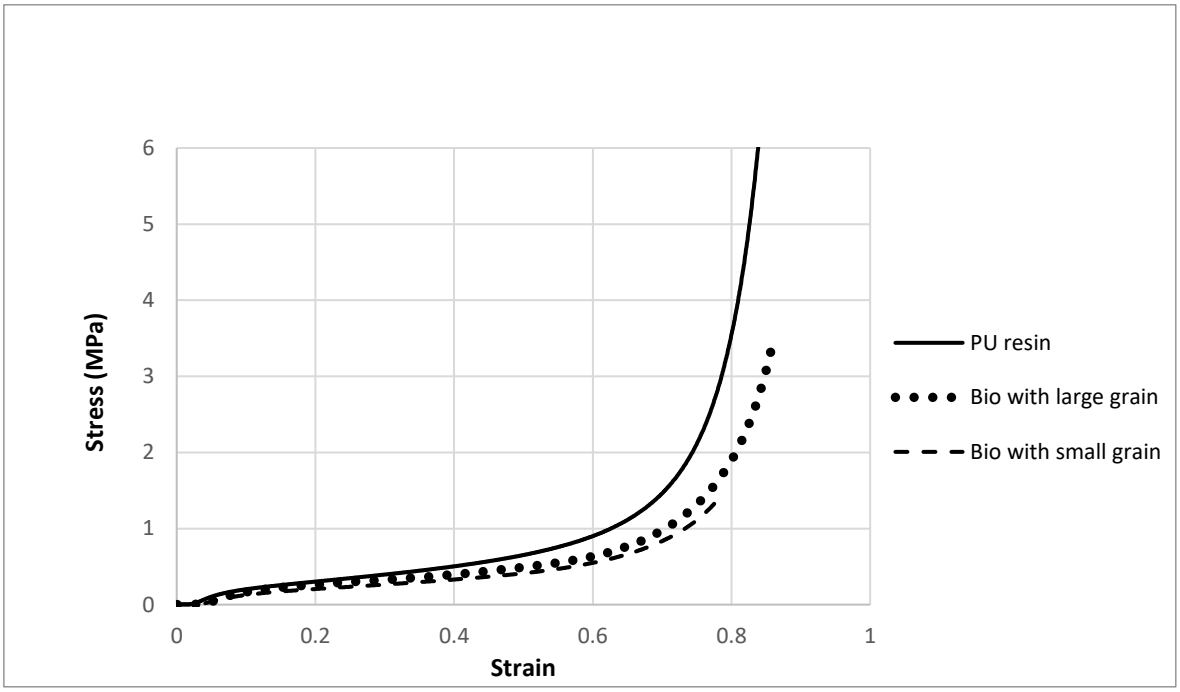

Figure 3.5: Influence of the bio binder agent and of the grain (equal density 160 kg/m^3).

3.2 Graphene reinforcement

To evaluate the effect of the introduction of graphene nanoplates (GNP) or graphene oxide (GO) on the agglomerated cork, it was analysed its behaviour under quasi-static compression tests. The only inconstant term of the equation was the percentage of the reinforcement used, which varied between 0.1, 0.5 and 1 wt. % for both GPN and GO (Figure 3.6). It is also important to refer that the binder used in this case is not the bio one tested previously, but the polyurethane-based one, provided by Flexpur.

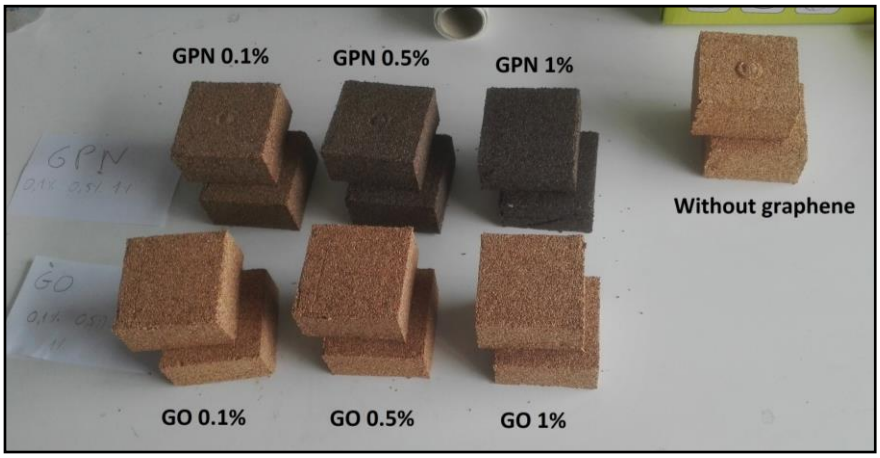

Figure 3.6: Graphene's campaign- seven different samples tested.

It was also made a control test without any reinforcement for scientific rigor purposes. Parameters such as density, percentage of binding agent, type of grain were kept equal throughout the entire time as it is possible to check accordingly with the table 8.

By observing figure 3.7 it can be seen that all the three samples with 0.1%, 0.5% and 1% of GO, plus the blank one, exhibit a similar performance until values of strain that are around 40%. From that point, it is possible to verify a pattern, since the ones with more graphene have longer plateau stages (but not higher) and, consequently, later densifications. These results show a gradual slight enhance in the mechanical properties of the agglomerate, as GO is added. However, it is important to say that the Young modulus does not change due to GO at any rate of reinforcement.

The most significant jumps in quality are given principally from 0 to 0.1 wt. % of GO and from 0.5 to 1 wt. % of GO.

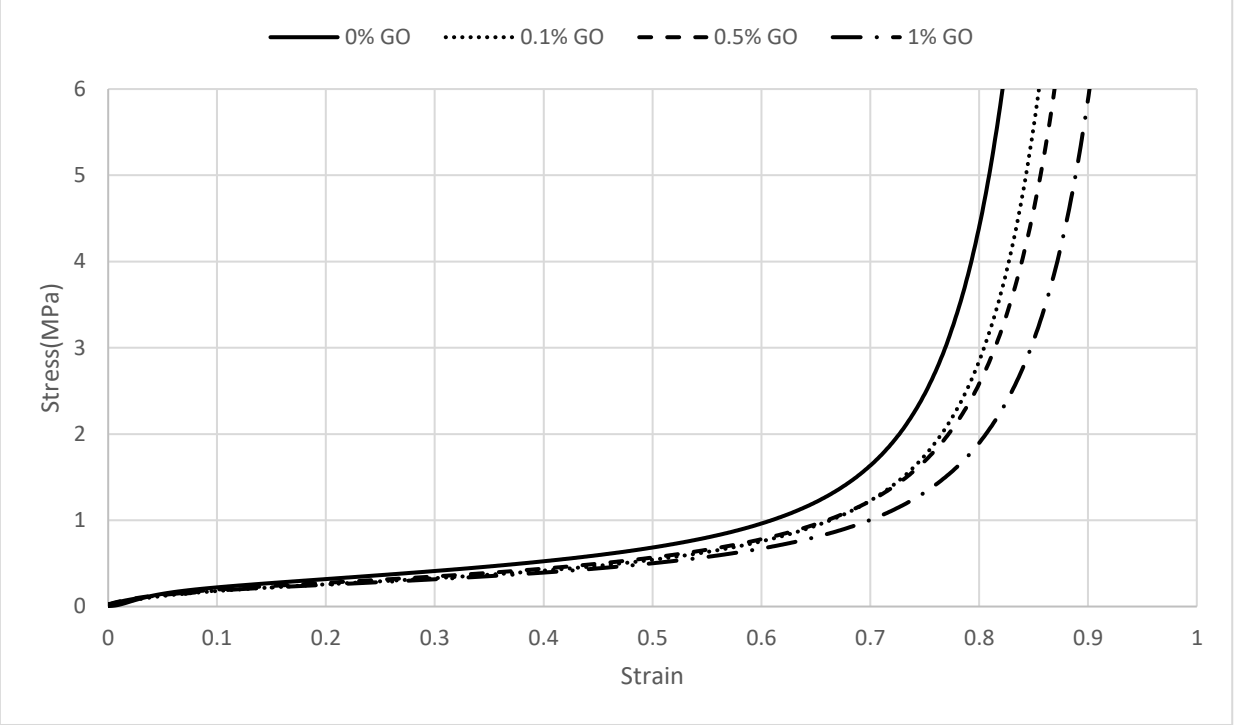

Figure 3.7: Influence of the GO used as a reinforcement (equal density 160kg/m^3 and grain used).

In the same way that was done the test with GO, also with GNP was produced three different types of samples of agglomerated cork, with the equal type of binding that was already described, the same density of 160 kg/m^3 and the same 10 wt.% of agglomerating agent. The difference was only present in the amount of GNPs used (0.1, 0.5 and 1 wt. %). The next figure (3.8) demonstrates a sample of 1 wt. % of GNP during a test.

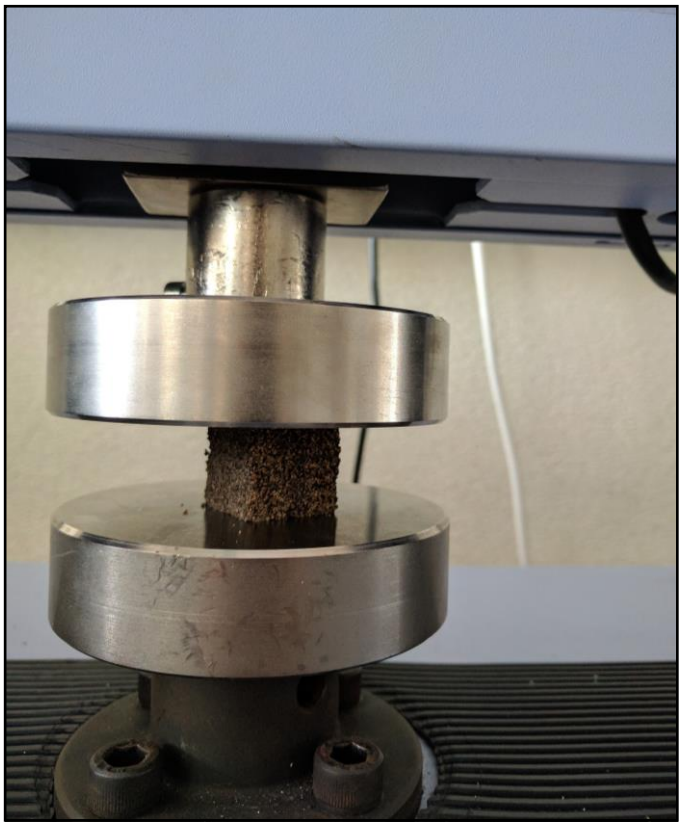

Figure 3.8: Sample with 1% GNP during the quasi static uniaxial compression test.

By analysing the figure 3.9, it is possible to deduce at first instance, that the results look similar to the ones with GO. Specifically at the beginning, nothing has changed. Until 40% of the total strain, the curves are close, and there is not any difference in Young modulus, again, by adding GNP in any percentage studied. After that, it is seen a regular increasing of mechanical properties, namely of plateau stress.

In engineering, as previously said for multiple times, the ambition goes through getting the higher amount of energy absorbed. If this is possible to be obtained in a stable momentum, (small variation of stress for different levels of strain) the better it is. For that reason, plateau effect is the most relevant moment of the stress-strain segment. From this particular point of view, samples with graphene are interesting once they last longer in this aspect. Despite that, they have the drawback of not getting higher values of stress during the plateau. Because of that, it can not be said that the levels of energy absorbed are higher with graphene.

The biggest difference, considering the studied range, happens from the blank sample to the one with 0.1 wt. % of graphene nanoplates, which stimulates the addition of this nanomaterial for any kind of composite meant to be used as reinforcement.

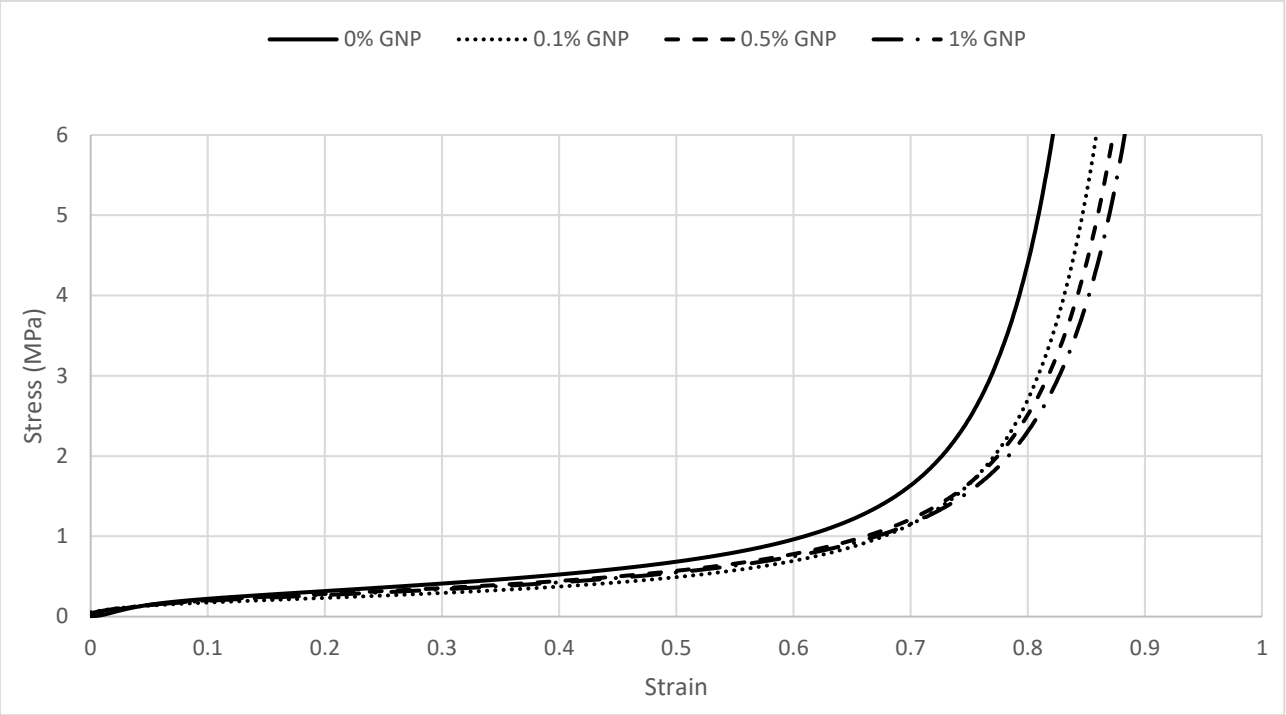

Figure 3.9: Influence of the GPNs used as a reinforcement (equal density 160kg/m^3 and grain used).

By examining the behaviour of the two carbon reinforcements (GNP and GO) and comparing them in equal percentages, some considerations can be taken. As it is possible to verify, for the amount of 0.1 and 0.5 wt. 1%, (Figure 3.10 and Figure 3.11) both GPNs and GO have similar performances when added to agglomerate cork samples, as it is possible to confirm since their stress-strain curves are practically coincident.

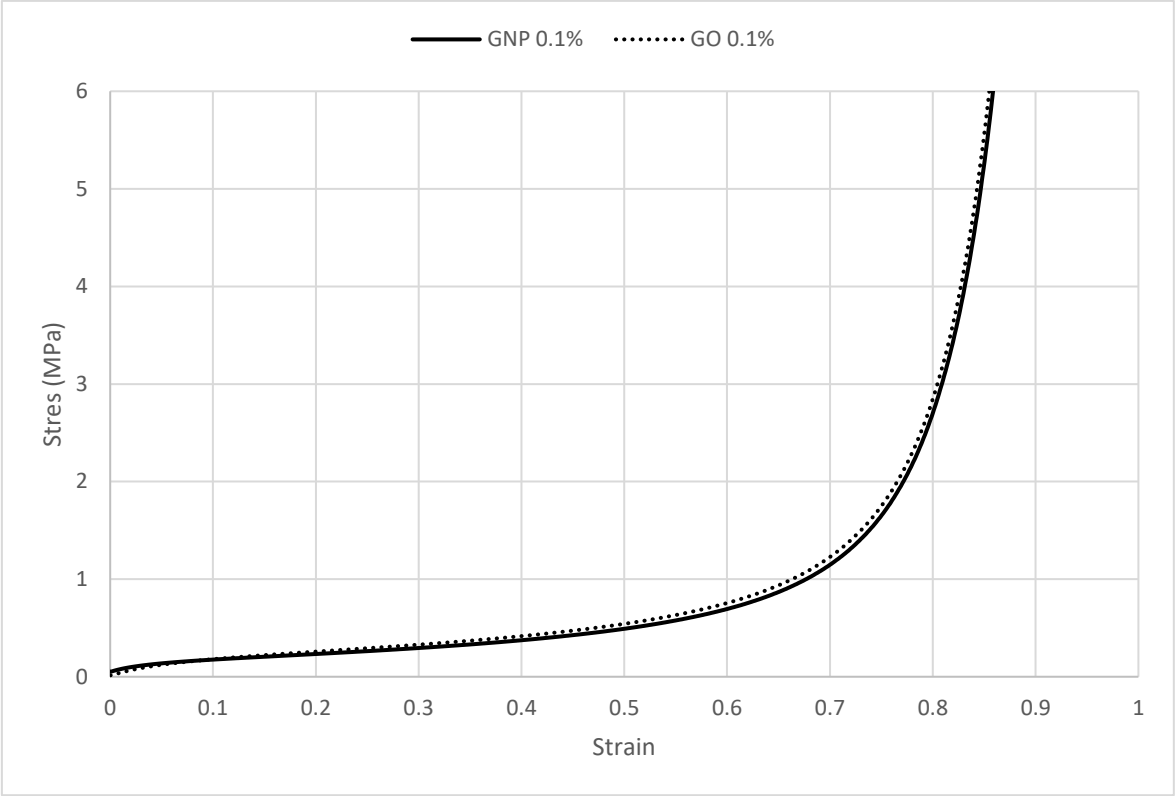

Figure 3.10: Comparison between samples with 0.1% GNP and 0.1% GO.

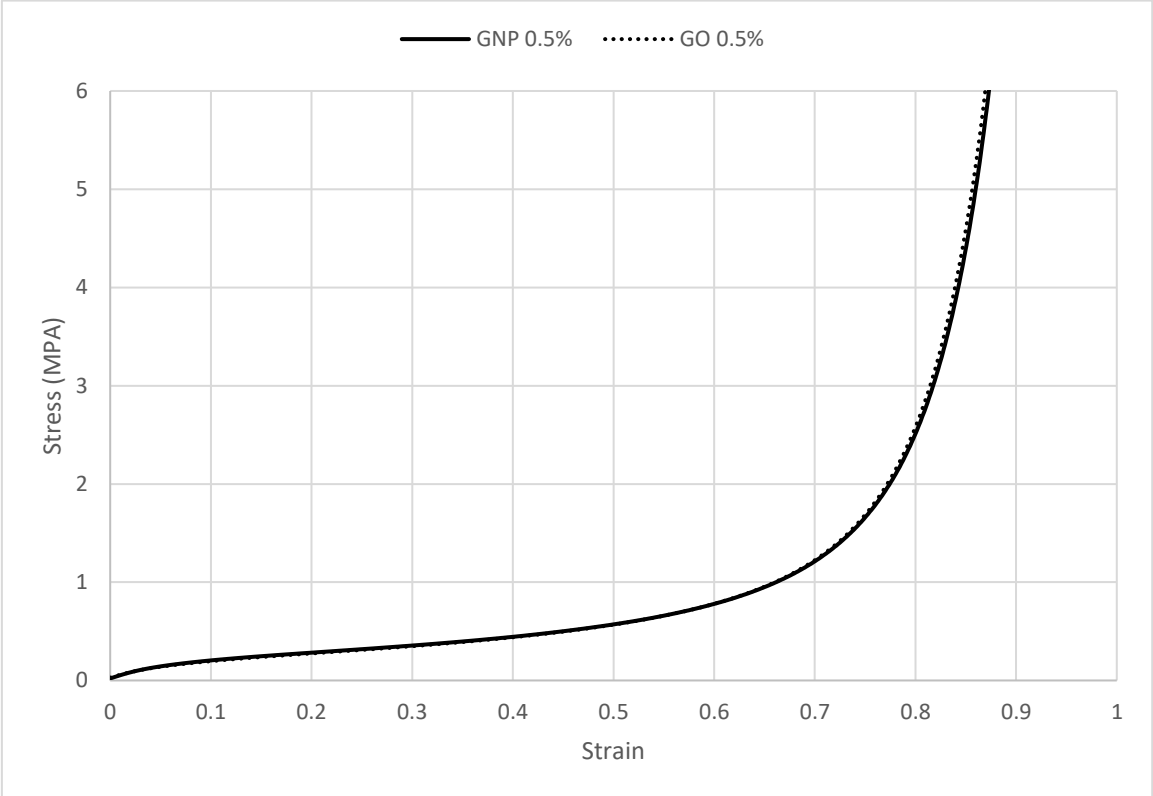

Figure 3.11: Comparison between samples with 0.5% GNP and 0.5% GO.

The biggest difference when comparing these reinforcements happens when the quantity added is 1 wt. %. As it is possible to see by examining the two curves (Figure 3.11), their course is slightly different. Meanwhile the sample with GNP has higher plateau, it densifies first. In relation to GO, it has a longer plateau, although that is not translated into gains at energy absorbed levels, once in that parameter the two options are equivalent.

The differences between these last examples analysed illustrate again, an idea that was already remarked before. It would be interesting to study these reinforcements in higher quantities, since most of the studied cases, it is when they appear in percentages above 0.5 that most variances show up.

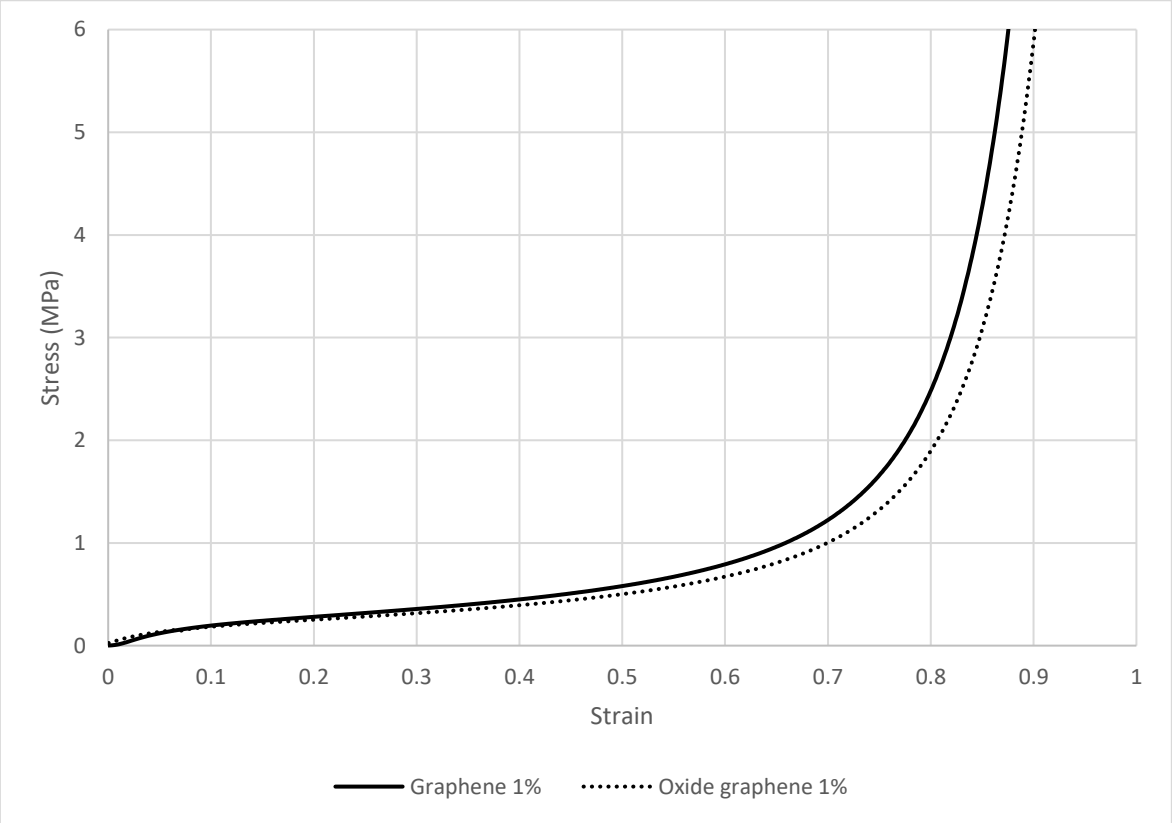

Figure 3.12: Comparison between samples with 1% GNP and 1% GO.

Chapter 4
Conclusions

This thesis starts a guideline to upgrade and launch a new direction in the processing of agglomerated cork in two different variants. In one hand it is intended to create a reinforced nanocomposite with GNP or GO, on the other it is aim to investigate a possible friendly way to meet the environment. In previous works, although graphene emerges as a big trend with multiple applications due to its properties, researches have been struggling to blend it into cork with success. Relatively to bio binders, it concerns a fresh mindset, frankly motivated by the recent increase of knowledge about such bio polymers, but also by the necessity of include them in a near future. This work explores these possibilities, creating new composites and testing their mechanical response. Not only validates the possibility of building a cork agglomerate with bio resin, but also tests the influence of nano reinforcement as GNP and GO.

Specifically speaking about the bio binders, it became clear the difficulty of creating a solid polymer. In order to make an integral composite with the bio resin used, the percentage of binder has to increase, comparing with synthetic versions. Mechanical tests allowed to infer that, although it is possible to produce bio samples with the behaviour of a cellular material in a stress-strain curve, they absorb less energy, once compared with synthetical ones.

Regarding the graphene composites, the delay of the densification was acquired, which turns out as a positive aspect, since it consequently extends the plateau stress. Many applications in engineering play with that advantage, becoming a useful resource, particularly when weight is a limitation. Nevertheless, the reinforcement with carbon nanostructures did not increase the energy absorbed, neither the Young's modulus, as someone with an ambitious mindset could be expecting.

For a future work around the issues addressed, several suggestions can be taken in consideration. Starting with the bio composites, the procedure needs to be enhanced. The amounts of chemical reactors used followed a recommendation present in the datasheets, but since this resin was never used to agglomerate cork, the quantities of the chemical initiator and accelerator can be improved. It is also possible to play with the mixing time and amount of binder, for example. Also, the curing conditions (time and temperature) for this type of resin must be optimized. This would modify the cure of the sample and could possibly bring better results. There is still a long way to go. In a more general perspective, the bio polymer used might not be the one with better characteristics to serve a purpose with such mechanical requirements. In fact, some studies suggest that the natural substitute

to PS or PU is the biopolymer PHA, namely the PHB version. Relatively to the graphene composites, it could be interesting to test higher percentages of this reinforcement, since the bigger differences observed were from 0.5 to 1%. The addition of the GO and GNP in the water instead of doing it directly on cork could also be a worthy try.

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Annex A

Datasheet of the used bio-binder granted by Resiquímica.

Characteristics

ERIS 140 is an unsaturated polyester resin of medium reactivity with a 54% content on renewable raw materials.

ERIS 140 has high stability to UV radiation.

ERIS 140 is allowed for use in contact with food.

Delivery Form

Approx. 67% of polymer diluted in styrene.

Applications

Cultured marble by cast process.

Specification

These technical data are determined in every batch. *

Viscosity at 25ºC Brookfield RVT (s21; 20 rpm)	500 - 600	mPa.s
MR 05 (ISO 2555)		
Gel Time at 80ºC 0,2% Co a 6% + 2% TBPB	5 - 10	min.
MR 10		

Additional Data

These data are not part of the product specification, being used solely to describe the product.

Polymer Content	66.5 - 68.5	%
MR 12 (ISO 3251)		
Acid Value	15 - 20	mg KOH/g
MR 08 (ISO 2114)		
Reactivity at 80ºC		
40ºC – T máx.	7 - 12	min.
T máx. 0,2% Co a 6% + 2% TBPB	195 - 205	ºC
MR 10		
Density at 20ºC	approx. 1.14	
MR 11 (ISO 2811-1)		
Flash Point	approx. 33	ºC
MR 13 (ISO 3679)		

MR – Resiquímica's Test Method

* Since this is an experimental product, deviations from the defined specification may occur.

Processing

ERIS 140 may be cured at room temperature by means of the addition of an accelerator (e.g. Cobalt) and an initiator (e.g. tert-Butyl peroxybenzoate - TBPB).

To obtain the ideal curing, it is recommended that the molded piece should not be used until 7 days after finished.

The application viscosity may be adjusted through the addition of styrene. Nevertheless, the data mentioned in this technical data sheet are not valid for this modification.

Properties of Cured Resin

Under determination.

Storage

ERIS 140 should be stored in the original and unopened containers and in the absence of light for no longer than 6 months at a temperature below 25°C. Higher temperatures may decrease significantly the storage stability.

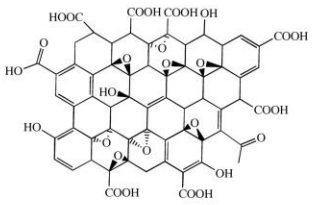
Safety and Environmental Protection

Please consult the Safety Data Sheet available on request.

www.resiquimica.pt Tel: +351 219 269 700 Fax: +351 219 269 780 July 2015

Datasheet of the used graphene oxide granted by Graphena.

Graphenea



Product Datasheet

Graphenea Graphene Oxide (GO)

Properties

Form	Dispersion of graphene oxide sheets
Particle size (nm, DLS)	600
Color	Yellow-brown
Odor	Odorless
Dispersibility	Polar solvents
Solvents	Water
Concentration	4 mg/mL
pH	2,2-2,5
Monolayer content (measured in 0.5mg/mL)	>95%*

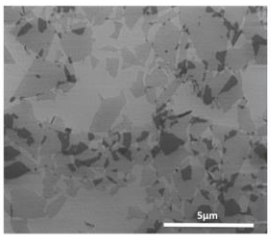
(*) 4mg/ml concentration tends to agglomerate the GO flakes and dilution followed by slight sonication is required in order to obtain a higher percentage of monolayer flakes

Elemental Analysis*

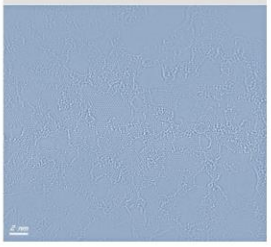
Carbon	49-56%
Hydrogen	0-1%
Nitrogen	0-1%
Sulfur	2-4%
Oxygen	41-50%

Sample preparation: 2g of 4wt% GO in water were dried under vacuum at 60°C overnight.

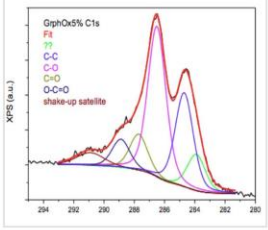
SEM image



TEM image



XPS



www.graphenea.com

Material safety data sheet of the used graphene nanoplates provided by Cheaptubes

Material Safety Data Sheet

acc. to OSHA and ANSI

1 - Identification of substance:

Chemical Name: Graphene Nanoplatelets
Formula: Carbon
Chemical Family: Synthetic Graphite
Synonyms: Graphene, Graphene Nanoplatelets, Few Layer Graphene Nanoplatlets, GNPs,
CAS Number: 7782-42-5 (Graphite)

- **Manufacturer/Supplier:**

Cheap Tubes Inc.
3992 Rte 121 E #3
Cambridgeport, VT 05141

(802) 869-5555

www.cheaptubes.com

Revision Date: April 13, 2015

2 - Composition/Data on components:

- **Chemical characterization:**
  Description: (CAS#)
  Graphite (CAS# 7782-42-5 , 95%)

Component	%	OSHA/PEL	ACGIH/TLV
Graphite	Up to 100%	15 mg/m3 (total dust) 5 mg/m3 (respirable fraction)	2 mg/m3 TWA
Metallic impurity	Balance		

*Exposure limits based on synthetic graphite

Material safety data sheet of the chemical accelerator, cobalt (II) 2-ethylhexanoate

SIGMA-ALDRICH sigma-aldrich.com

FICHA DE DADOS DE SEGURANÇA

de acordo com a Regulamento (CE) No. 1907/2006
Versão 5.6 Data de revisão 26.01.2016
Data de impressão 02.11.2017

SECÇÃO 1: Identificação da substância/mistura e da sociedade/empresa

1.1 Identificadores do produto

Nome do produto : Cobalt(II) 2-ethylhexanoate solution

Referência do Produto : 444545
Marca : Aldrich
No. REACH : Um número de registo não está disponível para esta substancia, já que a substancia ou os seus usos estão isentos do registo, a tonelagem anual não requere registo ou este registo está previsto para uma data posterior

1.2 Utilizações identificadas relevantes da substância ou mistura e utilizações desaconselhadas

Utilizações identificadas : Produtos químicos de laboratório, Fabrico de substâncias

1.3 Identificação do fornecedor da ficha de dados de segurança

Companhia : Sigma-Aldrich Química, S.L.
Sucursal em Portugal
Caixa Postal 131
Av. Almirante Gago Coutinho,
132-134,
P-2711 901 SINTRA

Telefone : +351219242555
Número de Fax : +351219242610
Email endereço : eurtechserv@sial.com

1.4 Número de telefone de emergência

Núnero de Telefone de Emergência: +(351)-308801773 (CHEMTREC)

SECÇÃO 2: Identificação dos perigos

2.1 Classificação da substância ou mistura

Classificação de acordo com el Regulamento (CE) 1272/2008
Líquidos inflamáveis (Categoria 3), H226
Irritação ocular (Categoria 2), H319
Sensibilização da pele (Categoria 1), H317
Toxicidade reprodutiva (Categoria 2), H361
Perigo de aspiração (Categoria 1), H304
Toxicidade aguda para o ambiente aquático (Categoria 1), H400
Toxicidade crónica para o ambiente aquático (Categoria 1), H410

Para o pleno texto das DECLARAÇÕES H mencionadas nesta Secção, ver a Secção 16.

2.2 Elementos do rótulo

Rotulagem de acordo com o Regulamento (CE) 1272/2008
Pictograma

Palavra-sinal: Perigo

Aldrich - 444545

Datasheet of the used chemical initiator (2-butanone peroxide)

SIGMA-ALDRICH®

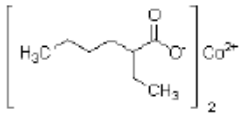
sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA
Website: www.sigmaaldrich.com
Email USA: techserv@sial.com
Outside USA: eurtechserv@sial.com

Product Specification

Product Name:
Cobalt(II) 2-ethylhexanoate solution - 65 wt. % in mineral spirits

Product Number:	**444545**
MDL:	MFCD00072632
Formula:	C16H30CoO4
Formula Weight:	345.34 g/mol



TEST	Specification
Appearance (Color)	Dark Blue to Very Dark Blue and Dark Purple to Very Dark Purple and Blue-Purple
Appearance (Form)	Liquid
Infrared spectrum	Conforms to Structure
Complexometric EDTA % Co	11.0 - 13.0 %

Specification: PRD.0.ZQ5.10000038710

Material safety data sheet of the chemical initiator (2-butanone peroxide)

SIGMA-ALDRICH sigma-aldrich.com

FICHA DE DADOS DE SEGURANÇA

de acordo com a Regulamento (CE) No. 1907/2006
Versão 5.5 Data de revisão 27.06.2016
Data de impressão 02.11.2017

SECÇÃO 1: Identificação da substância/mistura e da sociedade/empresa

1.1 Identificadores do produto

Nome do produto : 2-Butanone peroxide

Referência do Produto : 743003
Marca : Aldrich
No. REACH : Um número de registo não está disponível para esta substancia, já que a substancia ou os seus usos estão isentos do registo, a tonelagem anual não requere registo ou este registo está previsto para uma data posterior

1.2 Utilizações identificadas relevantes da substância ou mistura e utilizações desaconselhadas

Utilizações identificadas : Produtos químicos de laboratório, Fabrico de substâncias

1.3 Identificação do fornecedor da ficha de dados de segurança

Companhia : Sigma-Aldrich Química, S.L.
Sucursal em Portugal
Caixa Postal 131
Av. Almirante Gago Coutinho,
132-134,
P-2711 901 SINTRA

Telefone : +351219242555
Número de Fax : +351219242610
Email endereço : eurtechserv@sial.com

1.4 Número de telefone de emergência

Núnero de Telefone de Emergência +(351)-308801773 (CHEMTREC)

SECÇÃO 2: Identificação dos perigos

2.1 Classificação da substância ou mistura

Classificação de acordo com el Regulamento (CE) 1272/2008
Líquidos inflamáveis (Categoria 3), H226
Peróxidos orgânicos (Tipo D), H242
Toxicidade aguda, Oral (Categoria 4), H302
Corrosão cutânea (Categoria 1B), H314

Para o pleno texto das DECLARAÇÕES H mencionadas nesta Secção, ver a Secção 16.

2.2 Elementos do rótulo

Rotulagem de acordo com o Regulamento (CE) 1272/2008
Pictograma

Palavra-sinal Perigo

Declaração de perigo
H226 Líquido e vapor inflamáveis.
H242 Risco de incêndio sob a acção do calor.